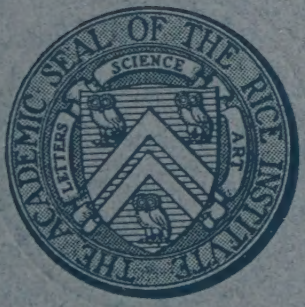
THE
RICE INSTITUTE
PAMPHLET

ol. XII January, 1925 No. 1



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THE RICE INSTITUTE PAMPHLET
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I

ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION [1]

THE first systematic observations of absorption spectra of organic compounds were made by Hartley and Huntington in 1879, and many substances were investigated by them.[2] The method of experiment consisted in photographing the spectrum of the light from the electric spark discharge between electrodes of an alloy of tin, lead, cadmium, and bismuth by means of a quartz spectrograph, a known thickness of a solution of the substance under investigation being placed in front of the slit. The spectrum of this alloy contains a considerable number of lines, and consequently it is an easy matter to detect absorption and measure its limits by comparing the photographs with one taken without the interposition of the absorption cell. The observations are necessarily restricted to the region of the spectrum which affects a photographic plate, and in Hartley and Huntington's investigations extended from the wave-length 5000 Angstroms to the wave-length 2200 Angstroms. The solvents used were water and methyl and ethyl alcohols, since it was found that these substances are diactinic to as far as 2200 Angstroms.

In an actual experiment a known thickness of a solution of a known concentration is used, and in this way a record

[1] A course of three lectures delivered by Professor E. C. C. Baly, C.B.E., M.Sc., F.R.S., of the University of Liverpool, in the Physics Amphitheatre of the Rice Institute, October 23, 24, and 25, 1924.

[2] Phil. Trans., *170*, 257 (1879).

is obtained of the absorption exerted by a definite molecular concentration of the substance under investigation. The molecular concentration is then reduced by decreasing either the thickness or the concentration of the solution, and a second photograph is taken. This procedure is followed until no measurable evidence of absorption is obtained. The wave-lengths or frequencies of the limits of absorption are measured on each photograph and plotted against the molecular concentration of the substance under investigation, and the absorption curve is thus obtained.

This method is essentially similar to that used at the present time, but the qualitative measurements of the limits of absorption has given place to an accurate quantitative determination of the absorptive power. By common consent the absorptive power is expressed in terms of the Bunsen and Roscoe extinction coefficient, $e = \log \frac{I_o}{I}$, where I^o and I are the intensities of the light before and after passing through the absorbing layer. Moreover, by the use of the modern panchromatic plates the limits of absorption have been extended to about 8000 Angstroms, and, also, it has been found possible with specially sensitive plates to reach as far as 1850 Angstroms in the ultra-violet. The latter is the extreme limit possible with a quartz spectrograph working in air, and for work on the absorption of light of smaller wave-length it will be necessary to use a vacuum grating spectrograph; but, up to the present time, no investigations of the absorption spectra of organic compounds have been made with this instrument.

The original investigations of Hartley and Huntington were continued over a long period by Hartley who published many papers on this subject. Following the usual custom of considering that molecules are characterised by

definite frequencies of vibration he gave the name of molecular vibration curves to his absorption spectra curves, and he noted that these seemed to be of two types and

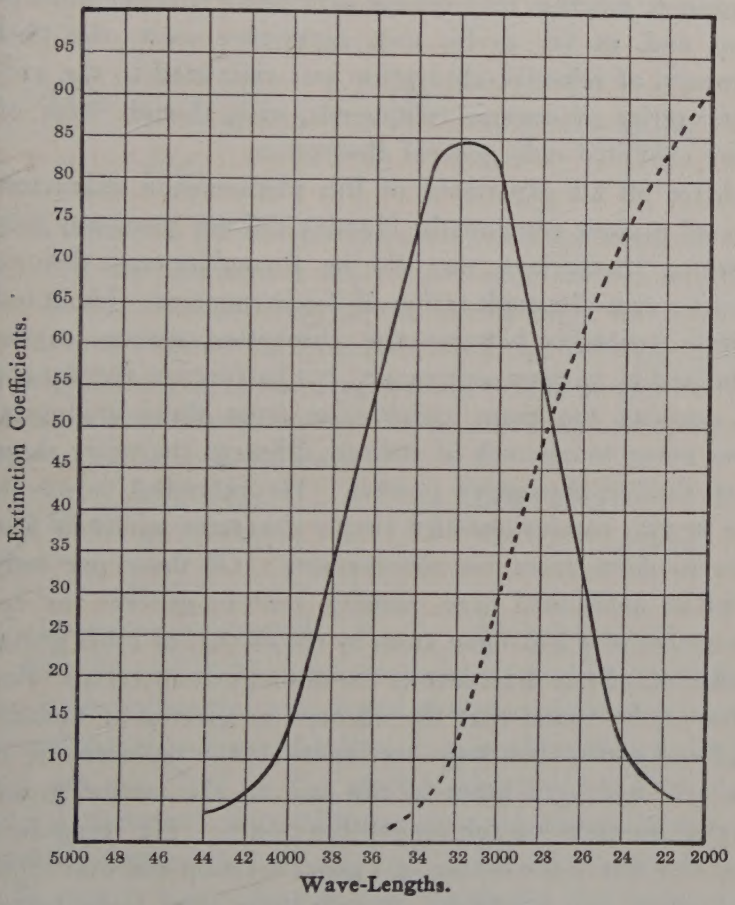


FIG. I.

that the absorption was either selective or general. In Fig. I the full curve A shows selective absorption with a well marked absorption band, as it is called, whilst the dotted curve B shows only general absorption; that is to

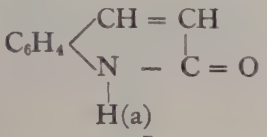
say, an absorptive power which steadily increases towards the shorter wave-lengths. Hartley considered that organic compounds could be broadly divided into two classes, according to whether they exhibit general or selective absorption; and, as far as his own experience went, the phenomenon of selective absorption was restricted to the aromatic series of organic compounds, even though some of these exhibited only general absorption.

After all his experience of this phenomenon characteristic of organic compounds, Hartley did not draw any far-reaching conclusions, nor did he formulate any definite theories as to the explanation of the phenomena. He noted certain analogies between the absorption spectra curves exhibited by various compounds; but he foresaw the danger of drawing too many conclusions from these analogies, since many compounds of entirely different character show very similar absorptive powers. He recorded, however, one or two conclusions of a simple character which he was able to draw from his observations. Of these one only need be mentioned here, namely, that in general the replacement of a hydrogen atom by the methyl or ethyl group makes very little difference in the absorption spectrum. For instance, he found that the absorption spectra of benzoic acid and methyl benzoate are identical, the replacement of the acid hydrogen atom of the acid by the methyl group having no effect on the absorptive power. He recognised that this was in the nature of a generalisation and that there are one or two exceptions, though these came to be better recognised as the experimental technique was improved.

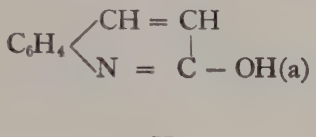
It was not long before Hartley saw the possibility of applying this generalisation to the determination of the constitution of a compound the methyl derivative of which possesses a known constitution. He foresaw the necessity

of caution in this new advance, and, indeed, the cases dealt with by him are very few in number.

The first instance of the application of this method was carbostyril, which may have either of the two formulæ, I and II.

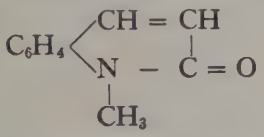


I

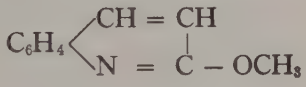


II

This substance gives in certain cases reactions which favour the first formula, and in other cases reactions which favour the second formula; one cannot decide from its chemical behaviour whether the hydrogen atom (a) is linked to the nitrogen atom or to the oxygen atom. The methyl derivatives of both substances are known and they can easily be proved to have the formulæ



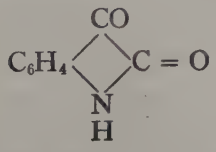
Methylpseudocarbostyril



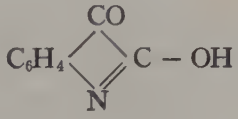
Methylcarbostyril

Hartley and Dobbie examined the absorption spectra of the three substances and found that the absorption curve of carbostyril agrees with that of methylpseudocarbostyril and not with that of the methylcarbostyril.[1] They concluded, therefore, that carbostyril has the ketonic structure shown in formula I.

In exactly the same way they concluded that isatin has the structure

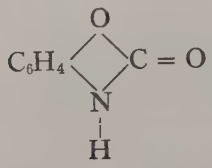


and not

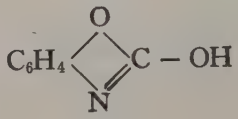


[1] Trans. Chem. Soc., *75*, 640 (1899).

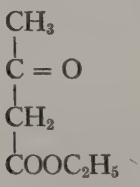
Hartley, Dobbie, and Paliatseas [1] examined the absorption spectra of *ortho*-oxycarbanil and by comparing it with the absorption spectra of the two alkyl derivatives concluded that it has the formula



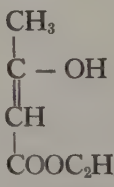
and not



A few years later attempts were made to apply this method to the settlement of the vexed question as to the constitution of ethyl acetoacetate by comparison of its absorption spectrum with those of its two ethyl derivatives, ethyl ethylacetoacetate, and ethyl β-ethoxycrotonate. It was then found that the problem is by no means as simple as had been previously supposed. Ethyl acetoacetate may exist in either of the forms I and II.

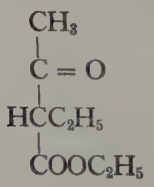


I. Ketonic

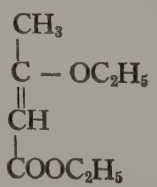


II. Enolic

and it was not possible from the chemical evidence to decide in which of these two formulæ it exists. Since the two isomeric ethyl derivatives are known to have the formulæ



and



[1] Trans. Chem. Soc., *77*, 839 (1900).

there seemed to be an admirable opportunity of applying Hartley's method of absorption spectra to decide the question of the constitution of the parent compound.

It was found, however, when the absorption spectra were examined, that the free ester and its metallic derivatives exhibit different absorptive powers from those of either of the two ethyl derivatives, the former showing selective absorption and the latter only general absorption.[1] This is a remarkable exception to Hartley's generalisation as to the substitution of a hydrogen atom by an alkyl group and justifies the conclusion that there is a marked difference in the free ester and its metallic derivatives compared with its two isomeric alkyl derivatives. The suggestion was put forward that the explanation of this difference might be found in the fact that the two alkyl derivatives possess fixed structures, whilst the free ester and its metallic derivatives might exist as equilibrium mixtures of the two desmotropic forms. On this view the selective absorption characteristic of the latter was attributed to the oscillating linkings involved in the equilibrium

This explanation appeared also to satisfy the selective absorption exhibited by other compounds possessing a labile or potentially labile hydrogen atom, such for instance as camphor in which the equilibrium was postulated

and acetone

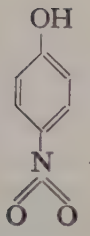
[1] Baly and Desch, Trans. Chem. Soc., *85*, 1039 (1904).

$$CH_3 - \underset{\underset{O}{\|}}{C} - CH_3 \quad \rightleftarrows \quad CH_2 = \underset{\underset{OH}{|}}{C} - CH_3$$

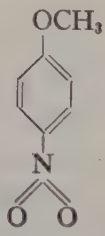
This theory had the further advantage in that it was able to explain the selective absorption exhibited by so many of the aromatic compounds, the oscillation being of the type expressed by the equilibrium between the two extremes of the Kekule formula

It may be noted in passing that this was the first attempt to find a physical explanation of the phenomenon of selective absorption.

It is not difficult to understand how it appeared possible to apply this theory of the origin of selective absorption to the determination of the constitution of certain aromatic compounds, such as the nitrophenols and their metallic derivatives. For some years previously the quinonoid theory of visible colour had been gaining ground, and on this theory the colour of the alkali metal salts of the nitrophenols was explained by their having the quinonoid structure. For instance *p*-nitrophenol and its ether, *p*-nitroanisole, are colourless substances, whereas the sodium salt is yellow and not very different in colour from *p*-benzoquinone. According to the quinonoid theory these substances possess the following formulæ

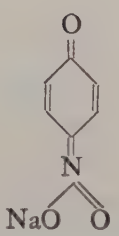


p-nitrophenol



p-nitroanisole

p-benzoquinone



p-nitrophenol sodium salt

Similarly, a quinonoid structure was given to the nitroanilines since the colour of these is very similar to that of the corresponding nitrophenol sodium salts.

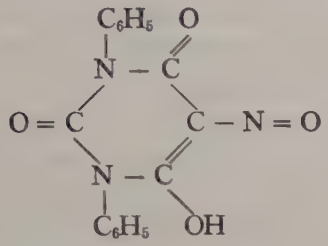
On the theory of the origin of selective absorption mentioned above, it seemed possible to settle the question of the constitution of the alkali metal salts of the nitrophenols, since it is to be expected that the oscillating linkings in the truly benzenoid nitrophenol would be different from those in the quinonoid structure. Absorption spectra observations showed that the nitrophenols exhibited absorption bands which differed materially from those given by their sodium salts, and, further, that the absorption spectra of the nitroanilines are very similar to those of the corresponding nitrophenol sodium salts.[1] This was accepted as evidence in favour of the quinonoid structure of the sodium salts of the nitrophenols and of the nitroanilines, and the argument was very materially strengthened when Hantzsch and Gorke described the preparation of unstable and highly coloured modifications of some nitroanisoles to which they gave the quinonoid structure.[2]

[1] Baly, Stewart, and Edwards, Trans. Chem. Soc., *89*, 514 (1906).
[2] Ber., *39*, 1073 (1906).

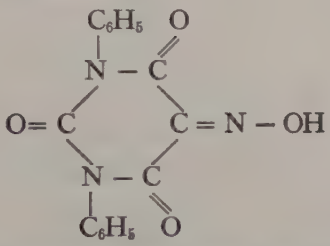
Further work was carried out on the three hydroxypyridines,[1] dimethylpyrone and some of its derivatives,[2] the hydroxyazo compounds,[3] the whole tending to confirm the view that there exists a definite correlation between chemical constitution and absorption spectra in the visible and ultra-violet regions, whatever might eventually prove to be the true physical explanation of selective absorption.

This theory was adopted by Hantzsch for reasons of a somewhat different kind, and a great wealth of material was added to the literature by him and his co-workers. Hantzsch developed the theory more rigidly by definitely connoting one absorption band and one structure. It is not possible to describe this work and the conclusions drawn, but one example may be quoted, namely, diphenylvioluric acid and its alkali metal salts.[4] The free acid dissolves in chloroform to form a colourless solution which exhibits an absorption band in the ultra-violet with central wave number of about 3740. The lithium salt, which is red, shows two bands with central wave numbers of about 1975 and 3210, whilst the blue cæsium salt shows two bands with central wave numbers of about 1690 and 3210. Owing to the fact that the aliphatic nitroso compounds are blue in colour, and that there is a slight resemblance in shape between their absorption curves and that of the blue cæsium salt, Hantzsch concludes that the constitution of the blue salts of diphenylvioluric acid is to be represented by the formula

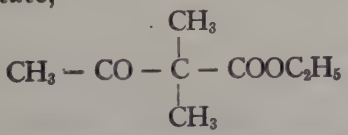
[1] Baker and Baly, Trans. Chem. Soc., *91*, 1122 (1907).
[2] Baly, Collie, and Watson, ibid., *95*, 144 (1909).
[3] Tuck, ibid., *91*, 449 (1907), *95*, 1809 (1909).
[4] Hantzsch and Robison, Ber., *43*, 45 (1910).



that of the free acid being

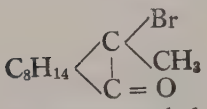


In the meantime results were being obtained in England which threw considerable doubt on the fundamental conceptions underlying the theory of correlation between chemical constitution and absorption spectra in the visible and ultra-violet regions. In the first place we have the theory, already mentioned, that an absorption band is due to an oscillation between two different linkings, a theory which is based on the observations made of the absorption spectra of ethyl acetoacetate and its derivatives. This theory received a severe blow when it was found that ethyl dimethylacetoacetate,

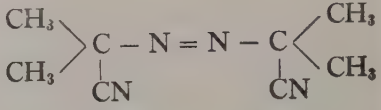


in which there is no labile hydrogen atom, exhibits a well marked absorption band in alcoholic solution in the presence of sodium ethoxide. Equally cogent criticism of this theory is found in the fact that many other compounds,

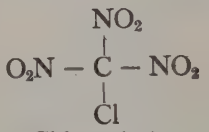
which contain no labile or potentially labile hydrogen atom, exhibit strong selective absorption. Amongst these compounds may be mentioned



αα′ Bromomethyl camphor



Azo*iso*butyronitrile



Chloropicrin

It is obvious, therefore, that the oscillating linking theory must be abandoned.

Then again, the quinonoid explanation of the change in absorption when the nitrophenols are converted into their alkali metal salts, and the quinonoid explanation of the absorption spectra of the nitroanilines could not be made to agree with the following observations:—

1. The absorption spectra of the nitroanilines are very similar to those of the corresponding nitrodimethylanilines, which are known to be benzenoid and not quinonoid.

2. The nitrophenols and their ethers in concentrated sulphuric acid solution exhibit colours which are very similar to those of the corresponding alkali metal salts, but the absorption spectra of the acid and alkaline solutions are materially different.

The second observation is very antagonistic to Hantzsch's theory that each absorption band denotes the presence of one definite structure. *Ortho*-nitrophenol exhibits two absorption bands in each of the three solvents alcohol, alcoholic sodium ethoxide, and concentrated sulphuric acid, and each of the six bands is at a different wave-length. It

is not possible to conceive that there can exist six different structures for one simple nitrophenol. Indeed, Hantzsch in one of his later papers remarks that he has found in certain cases more absorption bands than can be accounted for, that is to say some compounds exhibit more bands than the number of different structures which can be devised.

Perhaps the most damaging criticism of the Hantzsch theory is to be found in the fact that several compounds, for instance pyridine, piperidine, benzaldehyde, exhibit different absorption bands in the vapour and liquid phases. This is one of the most remarkable facts yet recorded, and it obviously is in strong opposition to the Hantzsch view, since it is not possible to believe that a substance, monomolecular in the liquid state, changes its structure when vapourised. Indeed, it is not too much to say that it is in direct opposition to any theory which connotes the primary structure of a compound with its absorption in the ultra-violet or visible regions.

A very important observation was made by Coblentz during his measurements of the absorption spectra of organic compounds in the infra-red region of the spectrum.[1] He noted that certain atomic groups such as CH_3, C_6H_5, NH_2, OH, CNS, give rise to definite absorption bands in the short-wave infra-red, and that these bands are quite independent of the rest of the molecule containing the group. The importance of this fact will be discussed in the next lecture, but it may be pointed out that this observation establishes a connection between groups of atoms independently of any question of structure. Thus, aniline and ammonia both show the characteristic absorption bands of the NH_2 group, and water, the aliphatic alcohols, and phenol all show the bands characteristic of the OH group.

[1] Pub. Carnegie Inst. Washington, No. 35 (1905).

It is not out of place here to draw attention to the remarkable arbitrariness of the structure-absorption correlation theory in that it attempts to establish such correlation from observations made in the visible and ultra-violet regions, which are such a minute fraction of the whole spectrum. It is now known that the frequencies characteristic of material substances extend over a very great range which in wave-lengths reaches from 30,000,000 Angstroms to 1 Angstrom, whereas the visible and ultra-violet regions extend from 8000 Angstroms to 2000 Angstroms, which is 1/5000th of the whole. It is inconceivable that any physical theory can be sound which is based on observations made in so minute a fraction of the whole range of frequencies known to be characteristic of all substances.

Sufficient has been said to indicate that many substances can exhibit different absorption bands under different conditions of temperature and solvent. To this it may be added that many substances exhibit two and even three absorption bands under the same conditions. In order to obtain as much information as possible about the various frequencies characteristic of compounds, numerous observations were made of the absorption spectra of a few substances, and attempts were made to correlate the various frequencies in each case. As will be seen from the full curve in Fig. I on page 3, the absorption band has a measurable breadth, but there is one frequency, known as the central frequency, for which the absorptive power is a maximum. It was found that, if the central frequencies characteristic of a given compound are considered, there exist constant differences between them. It seems necessary to conclude from this relationship between the characteristic frequencies that the different absorption bands must have their origin in different physical states of one and the

same molecule and not in different structural modifications. Indeed, we were driven to the conclusion that the accumulated evidence is definitely opposed to the structure-absorption correlation theory as far as the visible and ultra-violet regions are concerned, and so the theory was finally abandoned in spite of its attractiveness.

At this stage in the development of the subject there was no theory to take the place of the discarded theory, nor was there any explanation to hand of the origin of the absorption bands themselves. The first evidence which appeared to lead to a possible solution of the problem was obtained by a study of the absorption spectra of certain aminoaldehydes and aminoketones of the aromatic series and their hydrochlorides.[1] These compounds in alcoholic solution exhibit a well-marked absorption band in the ultra-violet, whilst the hydrochlorides obtained by the addition of excess of hydrochloric acid exhibit an absorption band with its centre shifted towards the shorter wave-lengths. If, however, an alcoholic solution of hydrogen chloride be slowly added to the alcoholic solution of the base, a visible colour is developed which reaches a maximum when from 0.1 to 0.2 equivalent of the acid has been added. This colour disappears when one equivalent of acid is present. The visible colour is due to the presence of a new absorption band situated on the red side of the band characteristic of the free base.

It is obvious from these results that the free base is not converted directly into the salt on the addition of the acid, but that it is first changed into an intermediate phase which is stable in the presence of small quantities of acid and is converted into the salt when the amount of acid present is increased. In the case of these particular compounds it

[1] Baly and Marsden, Trans. Chem. Soc., *93*, 2108 (1908).

was not found possible to obtain the whole of the base in the intermediate phase, since the absorption spectrum revealed the presence either of the free base or the hydrochloride along with the intermediate phase. In the case of the sulphonation of certain phenotic compounds the same phenomenon was observed, and here it was found possible to convert the whole of the parent phenol into the intermediate phase by solution in concentrated sulphuric acid.[1] In the cold this solution of the intermediate phase is quite stable, but on gently warming the intermediate phase passes into the sulphonic acid.

The question at once arises as to the nature of the intermediate phase, for we must determine whether it is a new substance, structurally different from, but isomeric with, the parent compound, or whether it is the same molecule in a different physical state. Of these two alternatives there is no doubt that the latter statement is nearer the truth, as indeed the previous evidence has tended to establish. Fortunately the question was answered when the fluorescence of the parent compounds was examined. Many of the parent compounds dealt with in the last two communications cited, exhibit this phenomenon, that is to say, when they are illuminated with those light rays which they absorb, they emit rays of a longer wave-length. It is perfectly possible to observe the fluorescence spectrum of these parent compounds, and the striking fact was noted that in every case the fluorescence spectrum of the parent substance is the same as the absorption spectrum of the intermediate phase. Obviously, therefore, the same frequencies are characteristic of the two, parent compound and intermediate phase, since the former emits and the latter absorbs the same rays. There can be no doubt, therefore,

[1] Baly and Rice, Trans. Chem. Soc., *101*, 1475 (1912).

that we must be dealing with the same molecule in the structural sense, the physical properties of which differ in the two states.

The establishment of the intimate connection between two phases of a given molecule, a connection which has been confirmed in a great number of instances, together with the constant difference between the central frequencies which are characteristic of all the phases of a given molecule, gives almost overwhelming support to the view provisionally put forward above, namely, that under different conditions of temperature and solvent a molecule can exist in different phases, the difference between them being of a physical nature and not chemical in the structural sense. To this may be added that each phase is characterised by its specific set of vibration frequencies which, in absorption spectra observations, are recognised as an absorption band.

Some evidence has also been adduced that the chemical reactivity of two phases is different since it has already been shown in the case of the amino-aldehydes that the free aldehyde does not give a salt with acid whilst the intermediate phase does. This difference in reactivity between the different phases of a given molecule is evidenced still more strongly by the phenols in the sulphonation reaction already mentioned. Let us consider, for example, the case of quinol dimethyl ether which reacts with sulphuric acid to give the sulphonic acid according to the equation

$$C_6H_4(OCH_3)_2 + H_2SO_4 = C_6H_3(OCH_3)_2(SO_3H) + H_2O.$$

The ether in alcoholic solution exhibits one absorption band with a central frequency of 1.035×10^{15} and if sulphuric acid be added to this solution no sulphonation will take place even though the molecular concentration of the acid be five times that of the ether. If, however, the ether be

dissolved in concentrated sulphuric acid, the solution exhibits two absorption bands with central frequencies of 6.69×10^{14} and 1.0875×10^{15} respectively. The ether, therefore, must now exist in a condition different from that obtaining in alcoholic solution, and in this condition sulphonation readily takes place since the reaction commences immediately the solution is warmed. Clearly, therefore, the reactivity of quinol dimethyl ether in the two solvents is different.

Another example of the difference in reactivity shown when the absorption spectra are different may be quoted, namely, benzaldehyde. This compound in alcoholic solution and concentrated sulphuric acid solution shows different absorption spectra. In alcoholic solution it is readily oxidised by atmospheric oxygen and is not sulphonated even when five times the molecular concentration of sulphuric acid is added. In concentrated sulphuric acid solution the aldehyde is not oxidised by atmospheric oxygen, but it readily undergoes sulphonation.

Instances of the change in reactivity associated with change in absorption spectra might be multiplied, but two examples are sufficient to establish the truth of this fact. We are justified, therefore, in concluding that under different conditions of temperature and solvent any given molecule may exist in one of a number of phases, each phase being characterised by its own characteristic frequency in the visible or ultra-violet region of the spectrum, and by its own reactivity. Further, the differences between the various frequencies characteristic of a molecule can be expressed as integral multiples of a constant difference.

Up to the present we have not discussed the question of the energy relations which must have a fundamental bearing on the problem, since the very fact that a substance

exhibits an absorption band at a definite frequency shows that it is capable of absorbing radiant energy of that frequency. The enunciation by Planck of the energy quantum theory enables us to consider the energy problems of absorption spectra and the relations between the various molecular phases in a quantitative way. There can be no doubt that when molecules are absorbing light their energy content is increased, at any rate temporarily, and, further, that if no chemical or physical change is permanently established thereby, the whole of the absorbed energy is again radiated to the surroundings. According to the energy quantum theory the absorption or emission of energy by a molecule is not a continuous process, but consists in the taking up or giving out of definite and fixed amounts of energy, these definite quantities being called energy quanta. If a molecule possesses a characteristic frequency ν, then, when it absorbs or emits energy at that frequency, the process consists in the absorption or radiation of a single quantum at a time, this quantum being $h\nu$ erg where h is a constant and has the value of 6.56×10^{-27}.

This conception can be applied in a very simple manner to the absorption of energy by a molecule under conditions when no permanent physical or chemical change is established and when its energy content is not permanently altered. Under these conditions it is obvious that the whole of the energy absorbed must be radiated to the surroundings. It is possible of course that the energy could be radiated at the same frequency as the absorbing frequency, a phenomenon known as optical resonance, but this is very uncommon. By far the more usual case is the radiation of the energy in the infra-red region, and it was commonly believed that the energy was frittered away, as it were, in the form of heat. It would seem, however, on the

energy quantum theory that this very unsatisfactory notion is untenable and that the radiation must take place in quanta at infra-red frequencies characteristic of the molecule. In order to guard against any possible misconception, it may be stated that every single substance possesses characteristic frequencies in the infra-red to as far as the limit of the spectrum previously stated to lie at about the wave-length of 3000μ or 30,000,000 Angstroms.

Let us consider the case of a single molecule with a characteristic frequency ν_1 in the ultra-violet and let this molecule absorb one quantum $h\nu_1$ erg. Under the prescribed conditions of no permanent physical or chemical change in the molecule this increment of energy will be radiated to the surroundings at smaller frequency in the infra-red characteristic of the molecule. The process will consist of the radiation of quanta at that infra-red frequency, and, since no energy can be destroyed, the total energy increment will be radiated as a whole number of these quanta. If the radiating frequency be ν_x then obviously we equate $xh\nu_x = h\nu_1$, where x is a positive integer. Dividing both sides by h we have $x\nu_x = \nu_1$ and, therefore, the absorbing frequency must be an integral multiple of the radiating frequency.

As has already been demonstrated, a substance may exhibit several absorption bands, depending on the phase in which the molecules exist. The above relation must hold for every such absorption band, the central frequencies being integral multiples of an infra-red frequency characteristic of the molecules. The simplest possible condition would be that all the frequencies characteristic of the molecule in the visible and ultra-violet are integral multiples of the same infra-red frequency characteristic of the molecule. If that were so, we should have $\nu_1 = a\nu_x$, $\nu_2 = b\nu_x$, $\nu_3 = c\nu_x$,

$\nu_4 = d\nu_x$, etc., where ν_1, ν_2, ν_3, ν_4, etc., are the visible and ultra-violet frequencies, ν_x is the fundamental infra-red frequency, and a, b, c, d, etc., are positive integers. It further follows that the frequency differences between the various visible and ultra-violet bands can be expressed in terms of a constant difference ν_x.

Now, it has already been shown that this relation does actually exist between the central frequencies of the various phases of a given molecule, and the question arises as to whether the central frequencies themselves are integral multiples of the constant difference. That this is actually the case has been conclusively proved in a great number of instances. As an instance of this the two absorption bands of pyridine may be quoted,[1] the true central frequencies of which are 1.0761×10^{15} and 1.1739×10^{15} respectively. The difference between these two values is 978×10^{13}, and $11 \times 9.78 \times 10^{13} = 1.0758 \times 10^{15}$ and $12 \times 9.78 \times 10^{13} = 1.1736 \times 10^{15}$, the differences between the calculated and observed frequencies being too small to be observed. If this relation has a sound physical basis the fundamental frequency in the infra-red will be capable of measurement by absorption spectra methods. The infra-red absorption spectra of pyridine vapour has not been observed, but liquid pyridine exhibits an absorption band at the frequency 4.8×10^{13}, which is very nearly half of 9.78×10^{13}.[2] This shows that the two absorbing frequencies in the ultra-violet should be expressed as $22 \times 4.89 \times 10^{13}$ and $24 \times 4.89 \times 10^{13}$, respectively. The case of pyridine is quoted, since, although only two absorption bands are known, the complete relation is proved by the independent observation of the fundamental band

[1] Baly and Tryhorn, Trans. Chem. Soc., *107*, 1121 (1915).
[2] Coblentz, loc. cit.

in the infra-red. Many cases are known in which the central frequencies of the several absorption bands shown by one substance are integral multiples of the constant frequency difference between them, no direct measurement of the infra-red absorption having been made. One such instance may be given, namely, isatin, the three absorption bands of which have central frequencies as follows

λ	Frequency	Difference	Factors
2430	1234.57×10^{12}		$1234.57 \times 10^{12} = 17 \times 72.62 \times 10^{12}$
		217.62×10^{12} which divided by $3 = 72.54 \times 10^{12}$.	
2950	1016.95×10^{12}		$1016.95 \times 10^{12} = 14 \times 72.64 \times 10^{12}$
		290.56×10^{12} which divided by $4 = 72.64 \times 10^{12}$.	
4130	726.39×10^{12}		$726.39 \times 10^{12} = 10 \times 72.64 \times 10^{12}$

It may be stated with some confidence that the existence of the above integral relationships and their direct connection with a single fundamental frequency in the infra-red establishes the reality of the various phases of a molecule which differ in physical properties and in reactivity. The question may well be asked as to what is the essential difference between the various phases. There seems little doubt that this difference is one of energy content, since it is possible to change a molecule from one phase into another, and indeed into a phase with smaller characteristic frequency by the supply of energy. This is shown clearly enough by the fact that when many substances are converted into vapour they undergo a change of phase which can be observed with the spectroscope, the new phase invariably being one with a smaller frequency. Then again substances are converted into phases with smaller frequency on exposure to light, but the new phase generally exists for too short a time for it to be recognised with the spectroscope. It is possible in some cases to introduce a second substance which increases the stability of the new phase and this phase can then be detected by its absorption spectrum. A typical case of this is trinitrobenzene which forms

a colourless solution in alcohol containing a trace of piperidine. On exposure to ultra-violet light the solution turns red owing to the development of a new absorption band in the blue region of the spectrum, and if this coloured solution is allowed to remain in the dark the colour vanishes and the trinitrobenzene reverts to its original phase.

An interesting extension of the integral relations discussed above may be deduced from the fact that the various phases of a given molecule differ in energy content and that the smaller the characteristic frequency of a phase, the larger is its energy content. The general case was dealt with of the absorption of a single quantum of energy by a molecule at a frequency in the visible or ultra-violet, and the radiation of this increment of energy as a whole number of quanta at the fundamental infra-red frequency of the molecule. This does not always take place, for at times the phenomenon of fluorescence is observed when some of the energy is radiated, not in the infra-red, but at a frequency characteristic of a phase of higher energy content and with smaller frequency than the initial phase of the molecule. Let a molecule absorb one quantum $h\nu_1$ and emit as fluorescence light at a smaller frequency ν_2 which is characteristic of another phase. The emitted light will consist of one quantum $h\nu_2$ and the difference $h\nu_1 - h\nu_2$ will obviously be emitted as quanta at the fundamental infra-red frequency ν_x. Since we know that $h\nu_1 = xh\nu_x$ and $h\nu_2 = yh\nu_x$, where x and y are positive integers, it follows that the difference in energy content of the two phases will be $h\nu_1 - h\nu_2 = (x - y)h\nu_x$. We thus arrive at the very interesting result that the difference in energy content of any two phases is equal to a whole number of quanta at the fundamental infra-red frequency of the molecule and that the difference between any two consecutive phases is one

fundamental infra-red quantum. This deduction is of considerable importance since we now have for the first time a quantitative definition of the various phases of a molecule. Every molecule exists in one of a number of possible energy levels or phases, the difference in energy content of any two consecutive phases being one energy quantum measured at the fundamental frequency of the molecule in the infra-red.

It can be understood from the foregoing that the phenomenon of fluorescence and the kindred phenomenon of phosphorescence are intimately connected with absorption spectra, but their physical significance does not seem to be generally understood. In the first place it is often stated that the two phenomena are identical in nature, the only difference being that phosphorescence persists for a measurable time after the source of exciting energy is removed, whilst fluorescence ceases instantly. This statement, however, does not seem to be true if the two terms are restricted, as they usually are, to radiation in the visible or ultra-violet regions of the spectrum. When molecules absorb energy at the frequency characteristic of the phase in which they exist, they may be converted into another phase of higher energy content. The increment of energy thereby gained is 1, 2, 3, or 4, etc., quanta at the molecular frequency, depending on which phase the molecule passes into. The difference between the quantum of energy absorbed and the increment of energy retained is radiated during the process. It is obvious that this difference is exactly equal to one quantum of energy at the frequency of the new phase, and this excess energy can be radiated either as one quantum at the frequency of the new phase, or as a whole number of quanta at the fundamental infra-red frequency. In the former case we have the phenomenon of fluorescence,

wherein the excess of the energy quantum absorbed, over and above the increment of energy retained by the molecule in its phase change, is radiated at the frequency of the new phase. The reverse process, during which the newly formed phase returns to the original phase, is accompanied by the evolution of the difference in energy content between the two phases as a few quanta at the fundamental frequency.

The phenomenon of phosphorescence is different in that the new phase has a measurable life period, very often lasting for protracted periods of time; and, further, the evolution of the phosphorescence is associated with the return of the new phase to the original phase, which is in fact the exact converse of fluorescence. In phosphorescence, just as in fluorescence, the energy is radiated at the characteristic frequency of the new phase, and a little consideration will show that there is a limit to the phase changes in which the phenomenon can be observed. Once again, let a molecule absorb one quantum $h\nu_1$ at its phase frequency, and let it thereby be converted into a new phase with frequency ν_2, the increment of energy retained by the molecule being as before $h\nu_1 - h\nu_2$. When the new phase reverts at a later date to the original phase, this energy increment is radiated as one or more quanta at the frequency characteristic of the new phase. We have, therefore, $h\nu_1 - h\nu_2 = xh\nu_2$ and $h\nu_2 = \frac{h\nu_1}{x+1}$, where $x = 1, 2, 3, 4$, etc.

It follows, from this, that the phenomenon of phosphorescence can only be observed when the frequency of the new phase is a sub-multiple of the frequency of the original phase.

The phenomena of phosphorescence and fluorescence have been discussed because it is possible by their means

to obtain valuable information as to the phase frequencies of molecules.

We may now sum up the information we have gained of the molecular phases.

1. A molecule exists in one of a number of possible phases.
2. Each phase is characterised by its own chemical reactivity and by its power of absorbing or radiating energy of definite frequency in the visible or ultra-violet region of the spectrum, this frequency being an integral multiple of a fundamental frequency characteristic of the molecule in the infra-red.
3. Each phase is characterised by its energy content, the difference in energy content between any two consecutive phases being one energy quantum measured at the fundamental infra-red frequency.

When a large number of molecules of a given compound are considered, it by no means can be assumed that they all must exist in one phase, and, indeed, the most usual condition is an equilibrium mixture between two or more phases. Many substances exhibit two, or even three, absorption bands in the visible or ultra-violet regions, and, in general, when only one band is shown in these regions there is definite proof that one or more bands exist in the extreme ultra-violet region, lying beyond the limit of the quartz spectrograph working in air. The proof of the existence of these bands with large frequencies is found in the well-known dispersion formulæ, which are based on the characteristic frequencies of the molecules.[1] This cannot be discussed now, but attention may be drawn in passing to the misleading nature of the statement that a substance only

[1] Baly, Astrophys. Journ., *47*, 28 (1915); Baly and Morton, J. Phys. Chem. *28*, 659 (1924).

exhibits general absorption. All this statement means is that the characteristic frequencies of the phases in which the molecules exist do not happen to lie in the visible or ultra-violet, but are in the extreme ultra-violet region.

The application of this theory to the problem of the interpretation of absorption spectra observations is quite straightforward. It is very obvious, in the first place, that the accumulated evidence may be accepted as having entirely disposed of the theory that there is any correlation between absorption bands and chemical constitution; and, in the second place, that the theory of the bands being due to oscillating linkings is also disproved. This evidence supports the view that a compound in the free state exists as an equilibrium mixture of two or more molecular phases, this equilibrium being dependent on the temperature of the system. This equilibrium is modified by the presence of a second substance, the amount of change depending mainly on the nature of that substance. Absorption spectra measurements give us a means of determining the phases which are present in the equilibrium in so far as the frequencies of the phases lie in the region of the spectrum observed, for it must not be forgotten that, very possibly, there are present phases, the frequencies of which lie in the extreme ultra-violet. It is not improbable that the relative intensities or absorptive powers measured at the characteristic frequencies are proportional to the relative number of molecules existing in those phases, although there is at present no absolute proof that this is true. It is possible that the dye-stuffs, which exhibit unusually high absorptive powers at their characteristic frequencies, exist very largely in that one phase. If so, this would give an explanation of their great colouring powers.

Of the instances already mentioned as having been used

in support of the structure-absorption correlation theory, two may be discussed in the light of the phase hypothesis—namely, the nitrophenols, and diphenylvioluric acid and its salts. In neutral alcoholic solution the nitrophenols exist as an equilibrium of two or more phases, and in alkaline solution a new equilibrium is established containing different phases; and, since one of these has a characteristic frequency in the visible region, the solution is visibly coloured. A third equilibrium exists when the nitrophenols are dissolved in concentrated sulphuric acid; and, again, one of the component phases has its frequency in the visible region, with the result that the solution is visibly coloured.

We may digress for a moment in order to discuss the application of the phase hypothesis to the existence of two modifications of the same compound. Many instances of this phenomenon are known in organic chemistry, and generally one modification is more stable than the other and has a higher melting point. According to the phase hypothesis, a pure compound, under a given condition of temperature, will exist as a definite equilibrium mixture of certain phases. There is no reason, however, why another equilibrium mixture might not exist in a metastable condition when solid compounds are considered. This metastable equilibrium mixture must be one of higher energy content, and would easily pass into the normal state with evolution of the excess energy. Since less energy will be required to convert the metastable solid equilibrium into the equilibrium characteristic of the liquid compound, the melting point of the unstable modification will be lower than that of the stable compound.

The existence of these metastable phase equilibria among inorganic compounds is well recognised, although, perhaps, the close connection between the phenomena in the two

fields of chemistry has not previously been emphasised. Many inorganic compounds on exposure to radiant energy, such as ultra-violet light or X-rays, exhibit the phenomenon of phosphorescence, that is to say, they acquire the power of emitting radiant energy which persists for a long time after the exciting cause has been removed. In some cases the energy increment is retained by the substance for an indefinitely long period, the phosphorescence not being developed until the substance is heated (thermoluminescence) or crushed (triboluminescence). This phenomenon finds a ready explanation in the phase theory, since the absorption of the energy establishes a metastable equilibrium between the phases present, which reverts to the normal equilibrium with the evolution of the excess energy, sometimes spontaneously, whilst at other times an external stimulus must be applied to initiate the escape of this energy.

In general it may be stated, if it be desired to prepare an unstable phase equilibrium and if the method of supplying radiant energy to the system is not possible, that the best method will be to prepare the substance under conditions which favour a phase equilibrium of higher energy content than the normal. For example, absorption spectra show that in its salts a nitrophenol exists in a phase equilibrium of higher energy content than the normal. When the ethers are prepared from these salts they must, at the moment of formation, exist in the equilibrium of higher energy content. If every precaution is taken to guard against change in this equilibrium, the nitrophenol ether will be obtained in an unstable form with an absorption spectra and colour similar to those of the original salt. It would seem highly probable, therefore, that the so-called *aci*-nitrophenols ethers of Hantzsch and Gorke [1] are not

[1] Loc. cit.

structural isomers of the normal ethers, but the normal ethers existing in a metastable phase equilibrium. The experimental conditions of their preparation are such as to favour the stability of the equilibrium with higher energy content, namely, the action of the alkyl halide at low temperatures on the carefully dried silver salt suspended in a non-aqueous solvent. Hantzsch and Gorke were unable to prove the quinonoid structure for these compounds, but based the formulæ on their colour, instability, and on the fact that they are monomolecular "isomers" of the normal ethers.

As previously pointed out, these compounds have been adduced as strong evidence in favour of the structure-absorption theory, but the phase hypothesis offers a different explanation and correlates them with similar metastable phase equilibria amongst both inorganic and organic compounds.

The various absorption bands exhibited by the alkali metal salts of diphenylvioluric acid, and interpreted by Hantzsch as evidence of different structural isomers, are very simply explained by the phase theory. The phase equilibria characteristic of this acid in its salts depend on the electropositivity of the metal. The greater the electropositivity, the higher the energy content of the equilibrium which is present, and the absorption bands exhibited by the various salts indicate the phases in which the acid exists in those salts.

In discussing the difference between the melting points of the stable and unstable modifications of a compound, I referred to the phase equilibrium characteristic of the compound in the liquid state. In view of the numerous cases known in which a vapour exhibits a different absorption band from the liquid, it is quite obvious that, at any rate

in these cases, there is a marked difference between the phase equilibria characteristic of the vapour and liquid states of the same compound. The latent heat of evaporation at the boiling point must, therefore, be a measure of the difference in energy content of the phase equilibria characteristic of the vapour and liquid at the boiling point. It has already been proved that the difference in energy content of any two consecutive phases of one molecule is exactly one quantum measured at the fundamental molecular frequency of that molecule, a quantum which may be called a molecular quantum. It follows, therefore, that the latent heat of evaporation must be a whole number of these molecular quanta. It might even be possible that, in some cases, the change from liquid to vapour at the boiling point be associated with the absorption of a whole number of molecular quanta by every molecule.

Now the size of the molecular quantum may be calculated from the frequency of the principal absorption band in the infra-red, and it is remarkable how accurately the molecular latent heat of vaporisation can be calculated in the case of some substances, the infra-red spectra of which have been measured. Whilst it cannot be claimed that in every case the molecular latent heat of vapourisation is the same whole number of quanta for every molecule, the agreement shown in the table on the following page is too close to be entirely fortuitous.[1]

In the cases of carbon tetrachloride and sulphur it may be noted that the infra-red measurements are not so trustworthy as those of the other compounds.[2]

Before concluding this discussion of absorption spectra and their interpretation, I must refer to Hartley's work

[1] Baly, Phil. Mag., *40*, 30 (1920).
[2] Coblentz, Pub. Carnegie Inst., Washington, No. 35 (1905).

HEAT OF VAPORISATION

	Observed molecular latent heat	Latent heat in ergs per molecule	Principal band in infra-red	Infra-red frequency	Quantum at infra-red frequency in ergs per molecule	Number of quanta	Calculated molecular latent heat
Carbon disulphide	6384	4.332×10^{-13}	4.6 μ	6.522×10^{13}	4.278×10^{-13}	1	6305
Water	9650	6.548×10^{-13}	6.115μ	4.906×10^{13}	3.218×10^{-13}	2	9485
Ammonia	4950	3.359×10^{-13}	12.04 μ	2.500×10^{13}	1.64×10^{-13}	2	4834
Acetic acid	5094	3.438×10^{-13}	11.5 μ	2.609×10^{13}	1.711×10^{-13}	2	5044
Methyl acetate	8166	5.541×10^{-13}	7.1 μ	4.225×10^{13}	2.772×10^{-13}	2	8170
Ether	6660	4.519×10^{-13}	8.75 μ	3.429×10^{13}	2.249×10^{-13}	2	6629
Chloroform	6984	4.739×10^{-13}	8.3 μ	3.614×10^{13}	2.371×10^{-13}	2	6988
Carbon tetrachloride ..	7190	4.879×10^{-13}	12.9 μ	2.326×10^{13}	1.526×10^{-13}	3	6744
Sulphur	23160	1.572×10^{-13}	11.8 μ	2.547×10^{13}	1.671×10^{-13}	9	22158

on the determination of the constitution of isatin, carbostyril, and *o*-oxycarbanil by comparison of their absorption spectra with those of their methyl ethers, for it might be considered that the theory now brought forward negatives the value of Hartley's evidence. This conclusion, however, by no means follows as a matter of course. If the two standards of reference show differences in absorption, a similarity between the absorption exerted by the parent compound and the absorption of one of the standards may be assumed to prove that the constitution of the two is similar. On the other hand, the availability of this method is very restricted, because observations made since Hartley's time have shown that phase changes sometimes take place on alkylation, which render the simple comparison of absorption spectra useless as a means of comparing two structures. A typical case, in which absorption spectra comparisons are useless, has already been mentioned, namely, ethyl acetoacetate and its alkyl derivatives. It is obvious that the parent ester must be ketonic, enolic, or a mixture of the two, yet its absorption spectrum differs from those of both of its alkyl derivatives and any mixture of the two. The reason for this difference is that the phase equilibria present in the free ester and its metallic derivatives are different from those characteristic of the alkyl derivatives, with the result that the simple comparison of their absorption spectra gives no immediate assistance to the chemist.

In conclusion I must emphasise the fact that, although the phase hypothesis offers an interpretation of absorption spectra and rests on a quantitative energy basis, there still remain to be filled many lacunæ in this theory. We do not know why a molecular phase is characterised by a frequency and by a specific reactivity. We do not know the origin

of the phases themselves, nor why the phases present so often vary with the solvent. The answers to these questions cannot be found from a study of absorption spectra alone. I believe, however, that they have been found from a consideration of the phenomena of chemical reaction and reactivity, but all discussion of this must be deferred until my next lecture.

II

A THEORY OF CHEMICAL REACTION AND REACTIVITY

THE expression of a chemical reaction by an equation which satisfactorily accounts for the numbers of the molecules taking part therein and the volumes of the reactants and resultants is too frequently accepted as being the last word on the subject. A somewhat sweeping statement perhaps, but I think it is justified when we consider how much is still left unexplained and how great is our ignorance of the fundamental phenomena of chemical change. We may select, as an instance, one of the simplest and most familiar of all reactions, namely, the combination of hydrogen and oxygen to form water, with its equation

$$2H_2 + O_2 = 2H_2O.$$

It is remarkable how small has been the increase in our knowledge of this reaction since the classic work of Gay Lussac and Humboldt. It is true that we have far more accurate information as to the exact volumes and masses of the components. It is true that we have learned the amount of energy lost in the reaction, but, in spite of these and other advances in our knowledge, the smallness of that knowledge becomes apparent when we consider how much we do not know of this reaction. We do not know why hydrogen and oxygen atoms combine together at all. We do not know how they combine, and we do not know why they do not combine instantaneously when mixed, but

require some external stimulus such as heat or an electric spark. I cannot but confess that these three questions to me present a fascinating problem, the solution of which would mean a great advance in our understanding of one of the most interesting of all natural phenomena, namely, chemical change.

In my previous lecture I indicated how some light was thrown on this problem by absorption spectra observations, because in two different reactions, namely, the conversion of the aromatic aminoaldehydes and aminoketones into their salts, and the sulphonation of the phenols, the first stage of the reaction consists in the conversion of the aldehyde, ketone, or phenol into an intermediate stage which then undergoes the expected reaction. The observations offer the additional evidence that this intermediate stage consists of the original substance with a definite increment of energy, the amount of which can be measured by the difference between the frequencies of the absorption bands of the compound in the two energy states. The existence of this intermediate phase of the reactant, with an energy content higher than the normal, is not represented in the recognised equation of the reaction; and thus we learn that an entirely novel phenomenon is associated with, at any rate, the two reactions mentioned. In short, the reaction consists of two separate and distinct stages.

During recent years considerable attention has been paid to the energy relations of chemical reactions, and the modern theory is that every chemical process is preceded by this preliminary stage in which the reactants, chemically inactive at the start, are rendered chemically reactive by the supply of a definite increment of energy to each of the molecules. I do not propose in this lecture to discuss the work which has led to this important generalisation, for

I wish to confine myself to a discussion of the phenomena of reaction and reactivity from the point of view of absorption spectra. With these observations as our starting point, it seems possible to formulate a theory which correlates reaction and reactivity with absorption spectra and offers an explanation of both sides of the problem.

It will be remembered that in the previous lecture I gave no explanation of the phenomenon of absorption, my reason for this being that, as long as there is no understanding of the origin of the characteristic frequencies of molecules, it is useless to attempt to explain absorption spectra. The customary practice of accepting these characteristic frequencies as the gift of nature to molecules is in itself highly unsatisfactory. It is often loosely stated that the frequencies in the extreme ultra-violet are due to the electrons, the frequencies in the visible and near ultra-violet to the component atoms, and those in the infra-red to the molecules. This statement does not help us at all, nor does it carry us any further, since the absorptive power must be due to the existence of free periods of vibration in the molecule; and it is difficult on this basis to account for the undoubted increase in the energy content of the molecule when it vibrates in sympathy with radiant energy of the same frequency.

Again, it is a well established fact that when two atoms combine together energy is lost in the process. When, for instance, an atom of sodium combines with an atom of chlorine, energy escapes to the surroundings and the molecule of sodium chloride contains less energy than the free atoms of sodium and chlorine. Where does that energy come from? It surely means that the atoms when in combination possess less energy than when they exist in the free state. Accepting the assumption that the free atoms

possess free periods of vibration it is not easy to understand how this enables those atoms to pass from a higher to a lower energy level. Further, we have yet to find an explanation of the fact, established by absorption spectra observations, that a molecule in passing from one phase to another changes its characteristic frequency.

These facts lead me to suggest that it is necessary to discard the theory of free periods of vibration as inadequate to explain well established phenomena. In my previous lecture I dealt with the integral relations between the various frequencies characteristic of a molecule, and I showed that their existence is an absolute necessity if the Planck hypothesis of energy quanta is sound. These relations, however, do not explain either the phenomenon of absorption or the Planck conception of quanta, yet they are observed facts, whilst the Planck quantum is only a hypothesis. For my own part, I believe that we shall approach more nearly to the truth if we postulate the exact converse of the commonly accepted theory. Whereas this theory postulates the existence of characteristic frequencies, and superimposed on that we have the Planck concept of energy quanta, I suggest that atoms and molecules are characterised by definite quantities of energy and that these determine the frequencies. In formulating this suggestion the observed facts of the integral relations between the absorption bands characteristic of a molecule are taken as the basis, and not the hypothesis of discontinuous radiation and emission as applied by Planck to the unexplained natural phenomenon of absorption bands.

The starting point of the new theory must obviously be the atom, since we have to account for the energy lost when two atoms combine together; and we, therefore, must state, as our principal assumption, that every atom is char-

acterised by a definite amount of energy which may be called the atomic quantum of energy. Every atom of the same element is characterised by the same atomic quantum, but the quanta of the atoms of different elements are different and characteristic of the elements. On this assumption an atom can only gain or lose energy in terms of its quantum, and it may be postulated that this quantum is associated with some physical change taking place within the atom, such, for example, as the shift of an electron from one stationary orbit to another.

In the second place, it may be assumed that this physical change within the atom takes a definite period of time which is the same for all atoms. Since the total energy absorbed is proportional to the frequency and the time, we may put

$$\frac{\text{Atomic Quantum}}{T} = \text{Frequency},$$

where T is a function of the time occupied by the physical change. It follows, from these two assumptions, that the atomic quantum endows the atom with the power of absorbing or radiating its quantum as radiant energy of a definite frequency, and the atom may be said to possess a characteristic frequency. These atomic quanta are very small and are of the order of 6×10^{-16} erg. The frequency established by these quanta is of the order of 9×10^{10}, the corresponding wave-length being about 3200μ.

Let us now consider the combination of two atoms together to form a binary molecule and let the characteristic quanta of these two atoms be 6×10^{-16} erg and 7×10^{-16} erg, respectively. Accepting it as an observed fact that energy is evolved in this process, we may attribute the phenomenon to the loss by the two atoms of a certain number of their atomic quanta, that is to say, the total energy loss

is shared in by the two atoms. In order to investigate the result of this it is necessary to have some basis to go on, and we may assume as a working hypothesis that the simplest possible sharing takes place, namely, that each atom contributes exactly half of the total energy loss. Two atoms, therefore, characterised by quanta equal to 6×10^{-16} erg and 7×10^{-16} erg, respectively, each lose the same amount of energy. The minimum amount of energy lost by each must be 7 quanta of the size 6×10^{-16} erg in the one case and 6 quanta of the size 7×10^{-16} in the other case. The total energy loss, therefore, is twice the least common integral multiple of the two atomic quanta and is equal to $2 \times 6 \times 7 \times 10^{-16} = 8.4 \times 10^{-15}$ erg. In order to resolve the resulting molecule back into its component atoms this quantity of energy must be absorbed by that molecule, and hence is characteristic of the molecule, since it is the quantity of energy required to decompose it. Similarly, if this molecule as a whole evolves energy, this must be a process in which its component atoms share equally, and hence the minimum quantity of energy which this molecule as a whole can absorb or radiate is 8.4×10^{-15} erg. This quantity of energy may therefore be called the molecular quantum, and hence the molecular quantum must always be based on the least common integral multiple of the quanta of its component atoms. A molecule, therefore, will be characterised by a specific frequency established by its molecular quantum, and this frequency may be called the fundamental molecular frequency.

According to this view the chemical combination of atoms consists in the joint loss of equal amounts of energy by those atoms, and we may postpone the consideration of the affinity between them which causes them to enter into this process. The important point at the moment is that

the theory can be put to the test of experimental observation. It is evident in the first place, on this theory, that chemical reaction can only take place between atoms which are capable of losing energy, and in the second place, that in entering into combination, atoms do not lose their individuality as absorbers or emitters of energy, for they still will be able to absorb or radiate their characteristic atomic quanta. On examination with the spectroscope a molecule will exhibit its own fundamental frequency and also those frequencies characteristic of its atoms, and the least common multiple principle should obtain between these. As a matter of fact, these relations have been observed and they afford striking evidence in support of the theory now brought forward.[1]

An important proviso must be made in connection with the atomic quanta and their least common multiples, since it is not possible to speak of the least common multiple of incommensurable quantities. In dealing with atomic quanta and in equating two amounts of energy, each consisting of an integral number of quanta, the tacit assumption was made that the two quanta were commensurable. It must not be forgotten, however, that these atomic quanta will not be commensurable unless they are expressed on the same fundamental scale. In order that they can be expressed on the same scale the atomic quanta must themselves be integral multiples of a fundamental unit of energy. It is impossible here to enter into the arguments which justify the existence of this fundamental unit, but they may be summed up by saying that did it not exist it would be utterly impossible to conceive of any correlation between the frequencies and energy contents of substances, and in-

[1] Baly, Astrophys. Journ., *42,* 1 (1915); Phil. Mag., *39,* 565 (1920); Garrett, ibid. *31,* 505 (1916); Baly and Garrett, ibid. *31,* 512 (1916).

deed the absorption of energy at one frequency and its radiation at another frequency would be impossible on the Planck theory.[1]

In dealing with the absorption by atoms of their atomic quanta of energy there is no need to assume that a single atom can only absorb one quantum at a time. It may absorb 1, 2, 3, etc., quanta at the same instant, and consequently atoms will exhibit a series of frequencies nA, where A is the frequency established by the atomic quanta and $n = 1, 2, 3$, etc. Since the probability of the atom doing this decreases with the number of quanta, the intensity of the absorbing frequencies nA will decrease with increase in the value of n. This is actually observed, and molecules exhibit series of atomic frequencies with decreasing intensity. The significance of the least common multiple will perhaps be better understood if we call the molecular frequency the convergence frequency of the series of atomic frequencies.

Up to the present we have only dealt with the combination of two atoms to form a binary molecule, each atom being assumed to be characterised by one atomic quantum. There is no need, however, to restrict our first assumption in this way for it is to be expected that, at any rate in the atoms of some elements, there will exist more than one possibility of shift of electrons, and that there will be associated with such atoms two or more atomic quanta of different sizes. When atoms of this type enter into combination, exactly the same conditions apply as in the case of the binary molecule dealt with above, but a fresh phenomenon makes its appearance. This may be understood at once if we consider the simple case of two atoms, A and B, combining together to form the molecule AB^2, A having two characteristic atomic quanta. Let the two atomic quanta

[1] Baly and Campbell, Phil. Mag., *41*, 711 (1921).

of A be represented by the numbers 2 and 3 respectively, and the atomic quantum of B by the number 5. As before, the fundamental molecular quantum of AB^2 will be based on the least common multiple of 2, 3, and 5, that is to say, 30, but we now have the possibility of two new quanta, namely, those of the atomic group AB. These two intra-molecular quanta, as they may be called, will be the least common multiples of 2 and 5, and of 3 and 5, respectively, one being caused by the combination of one atom of B by virtue of one atomic quantum of A, and the other by the combination of the second atom of B by virtue of the second quantum of A.

When such a compound is examined spectroscopically it will be found to exhibit three sets of frequencies, the fundamental molecular frequency, two intra-molecular frequencies, and three atomic frequencies. This type of absorption spectrum has been found in the case of water and sulphur dioxide, and the quantitative relations between the various frequencies conform to the theory with remarkable accuracy.[1]

There is no need to discuss in detail the relations which will obtain in more complex molecules, since, though possibly more complicated, the same principles will hold as in the simpler molecules. Two very interesting experimental confirmations of these relations may be mentioned. In the first place it is obvious that an intra-molecular quantum is solely characteristic of a particular group of atoms and can in no way be modified by the rest of the molecule. It follows, therefore, that all compounds containing such atomic groups as OH, NH_2, SO_3H, CH_3, C_6H_5, etc., will be characterised by the intra-molecular quanta of these groups and that they will show the frequencies character-

[1] Baly and Garrett, Phil. Mag., *31*, 512 (1916); Baly, ibid., *39*, 565 (1920).

istic of these groups. In my previous lecture I drew attention to the discovery by Coblentz of infra-red frequencies characteristic of these groups, these being shown by all compounds containing the groups.[1]

A second interesting combination is afforded by naphthalene which exhibits an intra-molecular frequency of 1.4136×10^{13} and this must be characteristic of an atomic grouping within the naphthalene molecule. The two chief atomic groups in this molecule are the benzene ring and the olefine grouping. The frequency 1.4136×10^{13} should be the fundamental molecular frequency of either benzene or the olefines, and, whilst no such frequency is found in the absorption spectrum of benzene, the characteristic frequency of the olefines is found from Coblentz's measurements to be 1.415×10^{13}.

There remains one further deduction which follows from this theory and leads to an important result from the point of view of the energy changes of a molecule. The fundamental molecular quantum is by definition equal to an integral number of atomic quanta characteristic of each of its component atoms, and is also equal to an integral number of the intra-molecular quanta characteristic of the groups of atoms forming part of the molecule. It follows, therefore, that a molecule can gain or emit one molecular quantum at any of those three frequencies. As will be seen later

[1] Pub. Carnegie Inst., Washington, No. *35* (1905). Time will not permit of the discussion of the principle of the combination of the various frequencies due to the simultaneous absorption of quanta of different sizes. In these combinations is found the explanation of the breadth and structure of absorption bands as actually observed. A full account of these will be found in the papers already referred to. These combined frequencies are of great importance as they enable us to determine the frequencies in the long wave infra-red where direct measurements have not yet been made.

this deduction is of singular importance in connection with the energy changes involved in a chemical reaction.

In the foregoing I have dealt only with the quantitative relations which follow from the original assumption that every elementary atom is characterised by one or more quanta of energy, the whole being based on an observed fact, namely, that there exists some force of attraction which causes atoms to come together and jointly to lose energy. It is not difficult to find an explanation of this affinity in the electro-magnetic force fields of the atoms as has been pointed out by Humphreys, Sir J. J. Thomson, and others, but the explanation lacked a quantitative basis. On the other hand it seems probable that the theory of atomic and molecular quanta is able to supply the necessary quantitative foundation. The electromagnetic force fields of atoms were first dealt with by Humphreys,[1] who showed that they are capable of giving a quantitative explanation of the Zeeman effect and also of the pressure-shift of spectrum lines. He deduced the fact that two atoms will attract one another when they approach in such a way that the direction of their electronic motions is the same, and will repel one another when their electronic motions are in opposite directions. Each atom, therefore, possesses two faces, and when one pair of faces comes together they attract one another, and when the other pair comes together they repel one another. In other words an atom forms the centre of an electro magnetic field of force, the opposite poles of which are localised in two opposite faces of the atoms.

Let it be supposed that two atoms of different elements are brought together in such a way that their mutually attracting faces come together. They will at once tend to form an addition complex, losing energy in the manner

[1] Astrophys. Journ., *33*, 233 (1906).

described above. The two atoms radiate equal amounts of energy as a whole number of elementary quanta, whereby the resulting molecule becomes endowed with a quantum based on the least common multiple of the atomic quanta. This molecule is now rendered a stable entity and can only be resolved into its atoms by absorbing an amount of energy equal to that lost in its formation.

As will be noticed, however, in this suggestion that the reactivity of atoms for one another is due to the attraction of their respective force fields and that their combination consists in their joint loss of equal amounts of energy, no account has been taken of the other faces of these combining atoms. Whereas the combination of the atoms produces a molecule characterised by a specific energy quantum, it is not possible to consider that the force fields due to the external atomic faces can exist without influence on one another. These external force lines must condense to form an external molecular force field and in this process energy must be radiated.

It was shown previously that a freshly synthesised molecule is characterised by a definite molecular quantum, and, therefore, when a freshly synthesised molecule loses energy as a whole it must do so in terms of its molecular quantum. It thus follows that, when the external force fields of the component atoms of a freshly synthesised molecule condense together to form the molecular force field, the system must lose a definite number of molecular quanta. Clearly the molecule itself will not suffer any loss of individuality as far as its characteristic quanta and frequencies are concerned. None of the deductions from the conception of elementary and molecular quanta made previously will be contradicted, and the only change accompanying the formation of the molecular force field will be the endowment

of the system with an additional quantum and frequency which are exact multiples of the fundamental molecular quantum and frequency, respectively. Let it be supposed that in the formation of its molecular force field a given molecule loses one molecular quantum. If the freshly synthesised molecule were allowed to absorb one molecular quantum, it would become endowed with certain properties. If, now, it is required to bring the molecule with its molecular force field established by the loss of one quantum into this physical state, it will be necessary to supply it with energy equal to two fundamental molecular quanta. There can be no reason against the molecule and its force field absorbing both these quanta simultaneously, and, therefore, it may be concluded that the system of molecule and force field becomes endowed with a new and additional quantum and frequency which are exactly twice the fundamental quantum and frequency. Similarly, it follows that if the force field condensation proceeds to the extent defined by the loss of two molecular quanta, the molecule and its force field will be endowed with a new and additional quantum and frequency which are exactly three times the fundamental quantum and frequency. Generally, if the fundamental quantum and frequency of a freshly synthesised molecule be denoted by M and $\surd$, and if in the formation of the force field x quanta are evolved, the system will be characterised by an additional quantum and frequency, namely, M $(x + 1)$ and $\surd$ $(x + 1)$, respectively. Since the external atomic fields are bound to undergo a certain amount of condensation, it is evident that the molecule must exist in one of a number of possible phases, each molecular phase being defined by the number of molecular quanta lost in the force field condensation, and characterised by a quantum and a frequency which are exact multiples of the funda-

mental quantum and frequency, respectively. Obviously, therefore, the difference in energy content between any two molecular phases will be one fundamental molecular quantum. It may be pointed out that the integral relationships between the frequencies and the existence of phases differing in energy content by one molecular quantum now deduced were also arrived at from absorption spectra observations as described in my previous lecture. The present theory, therefore, finds remarkable support in the experimental observations of absorption spectra.

In formulating our theory the initial assumption was made that the chemical reactivity of atoms is due to the attraction exerted by their electromagnetic fields. Similarly, the reactivity of molecules will be a function of their force fields, and it follows that the reactivity of a molecule will depend on the phase in which it exists. In other words, each phase will be characterised by its own reactivity, a conclusion that has also been independently arrived at from absorption spectra observations. Before attempting to apply this theory of molecular phases to the phenomena of chemical reaction and reactivity we may restate the whole theory and the deductions which have been made from it. The theory rests on three initial assumptions which are as follows:

1. Every elementary atom is characterised by one or more quanta of energy which are integral multiples of a fundamental unit of energy.
2. Atoms can only gain or lose energy in terms of their atomic quanta, and the process of emission or absorption of one quantum by an atom occupies a definite time which is the same for all atoms and may be equated to the Planck constant, 6.56×10^{-27}.

3. When atoms combine together the total energy loss is shared equally between them.

It follows, from these assumptions, that the quantum of energy characteristic of a molecule is based on the least common integral multiple of the quanta of its component atoms. Except in the case of binary molecules there will exist intra-molecular quanta, characteristic of groups of atoms within the molecule. The relations between the frequencies established by all these quanta have been directly observed experimentally.

The affinity or reactivity of atoms is attributed to their electromagnetic force fields, and, after atoms have combined together, their external force fields undergo condensation with the formation of an external molecular force field. This condensation takes place with the evolution of molecular quanta, and consequently a freshly synthesised molecule must pass into one of a number of possible phases, depending on the number of such quanta that are radiated. Each phase is characterised by its phase quantum and frequency, in addition to its molecular and atomic quanta and frequencies, by its specific reactivity, and by its energy content—any two consecutive phases differing in energy content by one molecular quantum. We thus arrive at conclusions which are identical with those drawn from absorption spectra observations.

In applying this theory to the phenomena of chemical reactivity and reaction we may first consider the case of elementary atoms, since it is necessary to discuss the probable nature of their force fields to which their reactivity is due. The simplest possible case will be that of an atom the electrons of which are rotating in orbits which lie in one plane. This will result in the establishment of an electromagnetic force field with its two poles equal and opposite. In this

case it is evident that condensation must occur between the force lines of each pole with the evolution of a large number of atomic quanta and the formation of a highly condensed external force field. Such an atom will, therefore, exist in a phase of abnormally low energy content and will possess no measurable reactivity. It may be suggested that the atoms of the rare gases, helium, neon, argon, krypton, and xenon, are of this type, and that the non-reactivity of these atoms is due to their force fields being completely closed. The present theory does not permit of there existing a condition of a zero valency, since it is impossible to conceive of an atom with no power of losing energy. If, however, the non-reactivity of these gases is due to the abnormal condition of their force fields, it follows that they should become endowed with reactivity if the closed force fields were opened by the supply of energy. The realisation of this would entail a large amount of energy being given to the atom, such as only could be supplied at the frequency characteristic of the highly condensed phase. This frequency must lie in the very extreme ultra-violet region, and radiation of that frequency will be absorbed by air, quartz, and probably by all known substances. Special means would, therefore, be necessary to supply this energy and the most likely condition would seem to be the electric discharge in vacuo. It is, therefore, of more than passing interest that so many observers have recorded the "disappearance" of the rare gases when an electric discharge is passed through them under reduced pressures. It certainly does not seem to be beyond the bounds of possibility that, under the influence of the electric discharge which is known to radiate energy of very short wave-length, the rare gases absorb this energy at their phase frequencies and are converted into

reactive phases with the result that they combine with the metal of the electrodes.

On the other hand, if there exist electronic orbits which do not all lie in the same plane, an unsymmetrical force field will result, and condensation to give the highly condensed and non-reactive external field will not be possible. The two poles will no longer be equal and opposite, and the strength of one or other will predominate. The atoms will tend to lose the maximum possible amount of energy, either by themselves or by combining with one another to form molecules. The normal state will be one in which the free particles are in radiant equilibrium with their surroundings. I believe that it will be possible, when the electronic orbits are known, to derive the various types of molecules with which the chemist is familiar, namely, (1) the non-reactive diatonic molecule such as H_2, N_2, etc., (2) the highly reactive monatomic molecule such as Na, K, etc., (3) the highly reactive diatomic molecule such as F_2, (4) the non-reactive polyatomic molecule such as that of carbon.

In the case of an incompletely closed external force field one pole will predominate and this will determine the nature of the reactivity of that element, whether it is electropositive or electronegative in type. Again, according to the theory of atomic quanta, an atom which is characterised by one quantum can only form a saturated molecule by combining with another atom of the same type. Such an atom will be univalent, whilst an atom characterised by two atomic quanta will have two powers of combining, that is to say it will be bivalent, and so on. The valency of an atom, therefore, would seem to be a measure of the number of atomic quanta characteristic of that atom.

When an atom is characterised by two or more atomic quanta, which must naturally be of different sizes, the

largest of these will be concerned first in any reaction, for it is safe to assume that a system will tend to fall to the lowest energy content possible under the conditions prevailing. In the case of such a molecule as $FeCl_3$ the energy lost in the three successive combinations of the iron atom with the chlorine atom will progressively decrease. The energy lost when the first atom of chlorine combines will be the least common multiple of the largest iron quantum and the quantum of chlorine. When the second atom combines the energy lost will be the least common multiple of the second iron quantum and the chlorine quantum, whilst in the third combination the smallest iron quantum will function. This is well known to be the case from thermochemical measurements. Following on this it may be suggested that the position of a metal in the electropositive series is determined by the numerical size of its largest characteristic atomic quantum.

When we come to consider the phases in which molecules exist, it by no means follows from the general theory that all the molecules of a given substance must exist in the same phase. The observations of absorption spectra described in the previous lecture, whatever interpretation be put on them, show very conclusively that some form of equilibrium exists which is changed by varying temperature and solvent. These equilibria, according to the present theory, exist between two or more phases of the given molecules, and in one or two cases it has been found possible to determine the relative amounts of the component phases. Thus chlorine at 0° and 760 mm. exists as an equilibrium mixture of two phases with absorption bands having centres at 3380.8 and 926.73 Angstroms, respectively, whilst the relative numbers of molecules in each phase are 10 and 3496.[1]

[1] Baly and Morton, J. Phys. Chem., *28*, 659 (1924).

In the case of solid substances the possibility arises of the metastable existence of equilibria which are different from the normal phase equilibrium. This phenomenon would be of particular interest in the case of the solid elements, since it would offer an explanation of allotropy. Smits has independently put forward the same theory in that he considers that allotropic modifications of an element are different equilibrium mixtures of a limited number of different molecular species of that element. In the case of sulphur Smits interprets the various allotropes as equilibrium mixtures of the four molecular species S_λ, S_μ, S_π, and S_ϕ. On the present theory the molecular species of Smits is a definite phase of the sulphur molecule; and we possess the added advantage of a more accurate knowledge of the criteria of the phases, for we know the energy content and the characteristic frequency of each phase. It becomes possible, therefore, to examine the equilibria existing in the various allotropes of sulphur by absorption spectrum methods, and by comparison with the four varieties to determine directly the components present. Some preliminary observations of these absorption spectra have given definite evidence of the truth of this interpretation of allotropy of sulphur, since the frequencies characteristic of the four varieties are also characteristic of the allotropic modifications. The problem of sulphur, however, is not so simple as it appears at first sight, and the investigation is being continued.

The molecular phase hypothesis may now be applied to the phenomenon of chemical reaction. Amongst the deductions from this hypothesis I mentioned that each phase of a given molecule is characterised by its own chemical reactivity, and hence for any given reaction a molecule must be brought into the right phase. If in the normal phase equi-

librium there are present no molecules in the appropriate phase, the substance will not react. Thus, in the instance quoted at the commencement of this lecture, namely, the combination of hydrogen and oxygen, there are present no molecules in the right phase and consequently no reaction takes place when the two gases are mixed.

In general, pure substances do not react with one another because no molecules in the appropriate phase are present. The well-known catalytic effect of certain impurities in promoting reaction will be discussed later. In actual fact, the molecules of pure substances exist in phases of lower energy content than the phase necessary for the reaction required. As a specific instance for detailed consideration we may select the reaction between hydrogen and chlorine which does not take place when the gases are mixed, the two phases known to be present in chlorine having no reactivity towards hydrogen. The reactive phase of chlorine has a larger energy content and by the supply of energy to the chlorine some of the molecules are converted into the reactive phase and the reaction commences. It is known that the two phases of chlorine absorb light of the wave-lengths 3380.8 and 926.73 Angstroms, and consequently rays of either wave-length should activate the chlorine molecules and induce the reaction with hydrogen to take place. Illumination of chlorine by the light of the shorter wave-length is not practicable in air, but it is well known that light of the longer wave-length causes the union of hydrogen and chlorine to take place.

Owing to the integral relationships which exist between the phase quanta and the fundamental quantum it should theoretically be possible to cause the necessary phase change in chlorine by exposing it to radiation of the same frequency as the infra-red fundamental frequency, which is

1.64325×10^{13} ($\lambda = 18.2565\mu$), since the phase change requires a whole number of the fundamental quanta. It must be remembered, if the phase change requires a large number of the fundamental quanta, that difficulties may arise. The probability against a single molecule absorbing a number of quanta increases with that number, since by the absorption of one quantum the molecule becomes a radiating system and therefore may lose that quantum before it absorbs the second. In the case of chlorine, however, the activation by infra-red radiation does seem to be possible, since the combination with hydrogen takes place when the mixed gases are heated.

The theory thus leads to the conclusion that in the case of all substances it is necessary to supply energy to the molecules in order to bring them into their reactive phases. Further, the amount of energy required for the phase change of any molecule depends on the energy contents of the initial and reactive phases and must always be exactly equal to a whole number of the fundamental molecular quantum. The molecular quantum of chlorine calculated from refractivity measurements is 1.078×10^{-13} erg per molecule, which is 1613 calories per gram molecule. The amount of energy required to activate a single molecule of chlorine must therefore be either 1.078×10^{-13} erg or some multiple of this.

The most important conclusion we have arrived at is that every chemical reaction must be preceded by a preliminary process in which the molecules of the reactants are activated. We see, therefore, that there must be at any rate two stages in every reaction, namely, activation and reaction proper. As a matter of fact, there is a third stage, as may readily be seen if we consider the reverse reaction, namely, the photochemical conversion of hydrogen chloride

into hydrogen and chlorine. The first stage in this reaction will be the absorption of energy by the hydrogen chloride molecules whereby they are changed from their normal non-reactive phases to their reactive phase. It follows that the reaction proper takes place between the reactive phases of the components from whichever side we start. In any reaction, therefore, there must be three stages, namely:

1. Absorption of energy to change the non-reactive phases into the reactive phase.
2. The reaction proper in which molecules of the products are formed in their reactive phases.
3. The loss of energy by the reactive phases of the products to give their normal and non-reactive phases.

It may be noted that the observed heat of any reaction, that is to say, the energy change that can be measured by means of a calorimeter, is the difference between the energy absorbed in the first stage and the energy radiated in the third stage. A reaction is endothermic or exothermic according to whether the first quantity of energy is greater or less than the second.

As described in the previous lecture, absorption spectra observations have definitely established the formation of the intermediate activated phase with larger energy content in two different reactions, namely, the conversion of certain organic bases into their salts and the sulphonation of certain phenolic compounds. These results are in exact agreement with the deductions made from the theory.

An important conclusion has been derived from the theory of the activation of molecules by a definite increment of energy as the preliminary stage of all reaction. If every molecule when activated by the definite increment of energy undergoes reaction, it follows that the number of molecules

reacting must be given by the total energy supplied divided by the definite increment. In the case of the photochemical reaction between hydrogen and chlorine, in which the chlorine is activated by light of its phase frequency in the ultraviolet, each chlorine molecule absorbs the phase quantum which is 5.821×10^{-12} erg. If the mixed gases absorb x ergs, then the number of chlorine molecules which react should be $x/5.821 \times 10^{-12}$ and the number of hydrogen chloride molecules formed should be $2x/5.821 \times 10^{-12}$. This is known as Einstein's law of photochemical equivalence.

As a matter of experimental fact it has been found that this law does not hold except in very few cases, the number of molecules reacting being enormously greater than one for every quantum absorbed. In some reactions as many as 10,000,000 molecules react for every quantum absorbed. This divergence from Einstein's law has been considered by many as a very serious criticism of any theory of chemical reaction based on the Planck energy quantum theory, but it would seem very probable on the present theory that the number of reactant molecules must greatly exceed the number of quanta absorbed in any exothermic reaction. The Einstein law is based on the first stage of the reaction only, and takes no account of the energy radiated during the third stage. This energy is radiated at frequencies characteristic of the resultants, and, since these contain the same elements as the reactants, some of this energy will be re-absorbed by the reactants with the result that more will be activated than the Einstein law requires. The proportion of the radiated energy that is re-absorbed will depend on the density of the radiation and on the density of the reactants. It has been experimentally proved that the divergence from Einstein's law does increase with increase

both in the density of the radiation and in the density of the reactant that is being activated. I believe that this affords the strongest possible evidence in support of the present theory. Further, it would follow that in an endothermic photochemical reaction the Einstein law should hold, since the energy available for re-absorption by the reactants is small. In the photochemical conversion of oxygen into ozone, an endothermic reaction, the law has been proved to hold good.[1]

This theory also offers an explanation of the variation in absorption spectra frequently observed with change in solvent, the variation being due to new phase equilibria being established. Since the absorption bands exhibited by one and the same compound under various conditions of temperature and solvent are characteristic of the different phases present, the integral relations between the frequencies should be in accordance with the present theory, and it has already been shown that they are exactly those required by the theory. No attention has as yet been directed to the mechanism whereby a solvent can supply energy to a substance and change the phase equilibrium. Let it be supposed that when a substance dissolves it forms an addition complex with the solvent molecules. There are two ways in which a complex of two or more molecules can be stabilised. The formation of the complex may be accompanied by the radiation of energy to the surroundings, in which case the complex cannot be dissociated unless that energy is restored to the system. On the other hand, a complex may be formed by the transference of one or more energy quanta from one component to the other, in which case the complex will not dissociate unless the amount of energy, equal to

[1] For a complete discussion of these phenomena see Phil. Mag., *40*, 23 (1920).

that transferred, is supplied to it. Absorption spectra measurements should show in either type of complex changes of phase compared with those present in the components. When a complex of the first type is formed both components lose energy, with the result that the phases present in the complex will exhibit a larger characteristic frequency than those shown by the free components. In the formation of the second type of complex one component gains energy at the expense of the other, and consequently the absorption spectra of the two will change in opposite senses. Any phase change on the part of one component will be accompanied by a corresponding phase change on the part of the other in the opposite direction. In this case the frequency characteristic of one component in the free state will shift towards the red, whilst the frequency characteristic of the other will shift towards the ultra-violet.

Some observations have been made of the absorption spectra of two liquid substances, the characteristic frequencies of which lie in the visible or ultra-violet, and of mixtures of the two, and the changes noted on mixing are exactly those expected on this hypothesis. The different phase of a given substance present in solution in different solvents may therefore be understood. It is very possible also that the phenomena of catalysis may be explained in the same way, the catalyst having the power of forming complexes with the catalyte, in which the catalyte is converted into the reactive phase required for the particular reaction that is accelerated.

The influence of the solvent molecules in changing the phase of a reactant need not be restricted to the cases in which a solution is actually formed, since the same conditions may apply to any mixture of substances. The re-

markable influence of water vapour in catalysing chemical reaction may well be due to the fact that it maintains some of the molecules of the reactant in the reactive phase. Since these form one component of an equilibrium mixture, the presence of very few will enable the reaction to take place. It is a necessary consequence that if every trace of water be removed, the activated phase of the reactant molecules will disappear from the equilibrium and the substance will become non-reactive. The loss of all power of reaction after intensive drying is a phenomenon made familiar to us all by the classic investigations of H. B. Baker, and in all probability the explanation is to be found in the fact that the water vapour when present converts some of the molecules into the reactive state. Here again the explanation can be put to the test of experiment, since, if it be correct, there will be definite evidence of a change in phase towards a condition of lower energy content on drying. Since the majority of the substances investigated by Baker only exhibit absorption bands in the extreme ultra-violet, the ordinary methods of absorption spectra are not suited for comparing the moist and dry substances. As has been previously stated the refractivity of a substance is connected with its characteristic frequencies in the extreme ultra-violet, and the refractivity will decrease if a phase change takes place accompanied by a loss of energy. It follows that the refractivity will decrease with intensive drying if the explanation now brought forward is correct. An investigation of the refractivities of moist and intensively dried gases is now being made in Liverpool, but the results although promising are not as yet ready for publication.

On the other hand, a very interesting positive result has been obtained with liquid benzene which shows a great decrease in refractivity on intensive drying. In the case of

liquids Baker has found a marked increase in the boiling point after intensive drying, and this is an obvious result if the drying causes the molecules to pass into a phase or phases of smaller energy content. Since the vapour obtained by boiling the two samples of benzene, ordinary and dry, is normal, a greater amount of energy must be supplied to the dried liquid to cause it to boil and consequently the boiling point will be higher. The refractivity of benzene can be expressed in terms of absorption bands in the ultraviolet, the frequencies of which are integral multiples of the frequency 1.5071×10^{13}. This, therefore, may be taken as the fundamental frequency of benzene and $1.5071 \times 10^{13} \times 6.56 \times 10^{-27} = 9.88666 \times 10^{-14}$ as the fundamental molecular quantum. If, therefore, every benzene molecule loses one molecular quantum on drying, the total amount of energy lost by one gram molecule will be $9.88666 \times 10^{-14} \times 6.22 \times 10^{23} \div 4.191 \times 10^{7} = 1467$ calories, and this extra amount of energy must be supplied to one gram molecule of the intensively dried benzene in order to cause it to boil. Now the specific heat of benzene at 94° is 0.481 calorie per gram or $0.481 \times 78 = 37.518$ calories per gram molecule and it follows that the energy increment of 1467 calories will raise the boiling point by $1467 \div 37.518 = 39.1°$. Since the boiling point of ordinary benzene is 80.1° the boiling point of the intensively dried benzene should be $80.1 + 39.1 = 119.2°$. In his original paper Baker stated that the boiling point is 118°, but more recently he has found the boiling point to be 119° which is strikingly close to the calculated value.[1]

In connection with the probability that the effect of intensive drying is to establish a new phase equilibrium of lower energy content, a brief reference may be made to

[1] Private communication.

some experiments on the thermal decomposition of ammonia.[1] It was found that ordinary ammonia dried by quick-lime requires much less heat energy to decompose it than does ammonia obtained by explosive evaporation of the liquefied gas. It was further found that traces of water vapour added to the gas dried by quick-lime materially reduces the amount of energy required to decompose it. So far as the effect of water vapour is concerned the results support the explanation given of the effect of intensive drying. As regards the smaller reactivity of the gas obtained by explosive evaporation of the liquefied gas, this is quite analogous to the cases of pyridine, piperidine, etc., the vapours of which exist in phases of higher energy content than those present in the liquid. If the same is true of ammonia, the gas obtained by explosive boiling of the liquid will contain phases of lower energy content than the normal gas, with the result that more energy will be required to decompose it.

Time does not permit me to quote many other experimental observations which support the theory, and, indeed, repetition tends to weariness. In spite of this there is one question which hardly can be avoided, namely, where does the ionic theory find a place in our theory? The answer to this question is a simple one for the phenomenon of ionisation may be a property characteristic of a specific molecular phase of an electrolyte. The molecular phase hypothesis attributes the reactivity of an electrolyte in solution not to the ions but to the molecular phase which forms those ions in the given solvent. The reactivity of an electrolyte will be the same in two solvents which maintain the same equilibrium of reactive phase, even if the amount of ionisation is different in the two solvents. This

[1] Baly and Duncan, Trans. Chem. Soc., *121*, 1008 (1922).

view has the advantage of correlating facts which on the ionic theory seem almost irreconcilable. For instance I need only mention the instantaneous and quantitative precipitation of copper chloride when benzene solutions of copper oleate and hydrogen chloride are brought together, the ionisation in the two solutions being negligible.[1] It must be admitted that the experimental proof is difficult, since in general the absorption bands of electrolytes are situated in the extreme ultra-violet and the refractivities of mixtures are not yet understood. On the other hand, we have indisputable evidence of the reactivity of the non-ionised molecules present in equilibrium with their ions. Perhaps also some results obtained in the absorption spectra measurements of violuric acid and its potassium salt in aqueous solution are of interest. It has always been believed that the colour of these solutions is due to the violuric ion, the colour being caused by a definite absorption band.[2] The absorptive power at the central frequency of that absorption band is proportional to the ionisation, which is exactly what would have been expected on the ionic theory or the molecular phase theory. If, however, a large amount of potassium nitrate be added to a solution of potassium violurate the absorptive power is not altered. This proves that the absorptive power is due to the reactive phase and not the violuric ion, since the ionisation of the potassium violurate is materially decreased by the addition of the potassium nitrate. Corroborative evidence may also be found in the observation by Garrison [3] that the conductivity of a suspension of copper coated with a thin layer of cuprous oxide is increased by light.

[1] Kahlenberg, Trans. Faraday Soc., *1*, 42 (1905).
[2] Donnan and Schneider, Trans. Chem. Soc., *95*, 956 (1909).
[3] J. Phys. Chem., *28*, 279 (1924).

In conclusion, may I say that in putting forward this theory of chemical reaction and reactivity I am fully aware that there is much experimental work yet to be carried out before it will be possible to say that it has fully stood the test of experiment? So far as the observations have been carried I have some confidence in saying that they uniformly support the theory. The deductions as to the existence of molecular phases and their properties made from absorption spectra observations are identical with those made from the theory. The support, however, given to the theory is found, not only in absorption spectra observations, but also in many other lines of work.

III

THE PHOTOSYNTHESIS OF NATURALLY OCCURRING COMPOUNDS

IN my second lecture I laid some stress on the fact that every chemical reaction must consist of three separate and distinct phases. Since molecules normally exist in non-reactive phases, it is necessary before any reaction can take place to convert these phases into the reactive phases by the supply of energy. The first stage of every reaction consists in the supply of a definite increment of energy to each molecule, this increment being determined by the difference in energy content of the reactive and non-reactive phases. This first stage is followed by the second stage or reaction proper, in which the reactive phases of the resultants are produced. The third stage consists of the loss of energy by the reactive phases of the resultants, whereby their normal or non-reactive phases are formed.

It follows from this development of our knowledge of chemical change that reactions may be divided into two classes, namely, those in which the increment of energy necessary for the activation of the reactant molecules is small and those in which this increment is large. This subdivision is very important, because the ordinary methods used in the laboratory for the activation of molecules, namely, the action of heat, solvent, or material catalyst, are only capable of supplying small quantities of energy and hence of stimulating reactions the necessary energy increment of which is small. The experience of chemists who

use these methods is, therefore, entirely restricted to this class of reaction, and as long as we continue only to use these methods we cannot gain knowledge of those reactions the necessary increment of which is large.

This latter class of reaction is, to a great extent, a new field, a study of which promises well, since results may be expected which are entirely outside the experience gained by a study of the former. In my two previous lectures I have brought forward evidence in favour of a specific reactivity peculiar to each phase of a given molecule. The reactivities of the phases of a molecule with large energy content will be very different from those of the phases of the same molecule with small energy content; and I feel, therefore, that I am fully justified in saying that, if it be found possible to carry out reactions of the second class, the results obtained will be of more than ordinary interest.

A moment's consideration will show that any highly endothermic reaction must belong to the second class, since it is obvious that the larger is the excess of the activating increment of energy over and above the energy radiated in the third stage, the greater must be that activating increment. In all probability, therefore, a reaction of the second class must be sought amongst the highly endothermic reactions.

The question arises as to the possibility of supplying in such a reaction the very large energy increment necessary to activate the molecules, since, as has already been pointed out, the ordinary methods of laboratory practice are unable to supply to any molecule the large number of molecular quanta which together make this critical increment. It might be considered possible to supply the large critical increment by working at a very high temperature such as that of the electric furnace, but this is impossible owing

to the fact that the products of the reaction will be unstable at those high temperatures. On the other hand the molecular phase hypothesis at once suggests a method of supplying the necessary energy increment which is free from the difficulties caused by intensely high temperatures. If the energy is supplied to the reactant molecules at the frequency characteristic of their non-reactive phase, the energy so gained will be sufficient to activate them for any reaction, however endothermic this may be, since it may readily be proved that the energy quantum characteristic of a phase is sufficient just to resolve it into its component atoms. From the theoretical point of view, therefore, it should be possible to bring about any reaction, even a highly endothermic one, by activating the molecules by light of the same frequency as that characteristic of the phases of the reactants which are present.

A typical endothermic reaction is the conversion of carbonic acid into formaldehyde and oxygen, since the reverse reaction, the combination of oxygen with formaldehyde to form carbon dioxide and water, evolves about 127,000 calories per gram molecule. It is known that carbonic acid exhibits an absorption band with a central wave-length of about 2000 Angstroms and the energy quantum characteristic of that phase is 9.84×10^{-12} erg which corresponds to 144,000 calories per gram molecule. This is a measure of the energy absorbed by carbonic acid when exposed to light of the wave-length 2000 Angstroms and is much larger than the observed heat of the reaction. It follows that we have at hand in the absorption of light at the phase frequency a method of supplying the energy necessary to activate the molecules in a reaction of the second class, a method which is theoretically ideal in the sense that the activated molecules of the product are able at once to lose

their energy to the surroundings, which would not be the case if the reaction were carried out at very high temperatures. It will, however, be seen later that this ideal condition has not as yet been entirely realised in the laboratory.

The conversion of carbonic acid into formaldehyde has an added interest, since it has long been believed that this reaction forms the first stage in the photo-assimilation of carbon dioxide by the leaves of living plants whereby starches, sugars, etc., are synthesised. The observations made by Willstätter, that the molecular ratio of the oxygen transpired and of the carbon dioxide absorbed by leaves during photo-assimilation is unity, have been generally accepted as a proof of the formation of formaldehyde as the first product. For this reason the reaction in question is the fundamental reaction of all life, and its realisation in the laboratory becomes doubly important. It must, however, be remembered that the presence of formaldehyde has never been established in the living leaf; and there is no doubt that this fact introduces an element of considerable difficulty, since previous experience would lead us to believe, if a definite substance is formed in the first of a series of reactions, that the presence of that substance would be capable of detection, especially in the case of formaldehyde, the tests for which are peculiarly delicate.

Some years ago Moore and Webster investigated the action of ultra-violet light upon aqueous solutions of carbon dioxide and found that formaldehyde in small quantities was formed, but that this only occurred in presence of certain inorganic catalysts, such as colloidal ferric hydroxide, etc.[1] They argued from this that a catalyst is necessary for the photochemical reaction and suggested that

[1] Proc. Roy. Soc., *87, B,* 163 (1914).

the importance of iron in the growth of a plant is to be found in this catalytic action. On the other hand, the necessity for a catalyst seems to be contrary to the theory, since the light energy alone should be able to promote the reaction without any further energy supplied by a catalyst. In spite of the negative results obtained by Moore and Webster the reaction was again investigated at Liverpool.[1] Carbon dioxide, prepared from pure calcium carbonate and synthetic hydrochloric acid, was passed through pure water contained in quartz test tubes, 8 x 1 inches, which were exposed to the light from a 220-volt quartz mercury lamp. Great care was taken to protect the carbonic acid solution from contamination by dust or any other impurities. It was then found that, if the distance between the lamp and test tubes was not less than 8 inches, small quantities of formaldehyde could always be detected in the solutions after twelve hours illumination. The presence of the formaldehyde was qualitatively proved by the Schryver test and the orcinol test, each of which is certainly capable of detecting the presence of one part in 1,000,000 parts of water. The amount of formaldehyde found was very small and was about 5 parts in 1,000,000, but there was no doubt whatever of its photochemical production from the carbonic acid.

In part at any rate the smallness of the yield of formaldehyde in these experiments is to be explained by the fact that formaldehyde is decomposed by very short wavelength radiations which are present in the light from the quartz mercury lamp. If dilute aqueous solutions of formaldehyde are exposed to this light, the formaldehyde is slowly decomposed, and after some hours no organic compound is to be found in the solution. It is evident, there-

[1] Baly, Heilbron, Barker, Trans. Chem. Soc., *119*, 1025 (1921).

fore, that when the rays from the quartz mercury lamp act on a solution of carbonic acid the formaldehyde produced undergoes decomposition, with the result that the amount present at any time can only be the excess of that formed over that decomposed, and this excess is very small. It is known that the destruction of the formaldehyde is caused by the very short wave-length light, since the interposition of a screen of calcite which absorbs these rays lessens the amount of decomposition. Unfortunately this screen also absorbs to a considerable extent the rays which activate carbonic acid, and, therefore, little benefit is gained by the use of such a screen between the lamp and the quartz tubes containing the carbonic acid.

The very short wave-length light is absorbed by air to a certain extent, so that its effect is diminished when the reaction vessels are placed at some distance from the lamp. This, no doubt, explains the negative results obtained by Moore and Webster with pure carbonic acid, since we found no evidence of formaldehyde when the distance between lamp and quartz test tubes was less than 8 inches.

It will be realised, therefore, that the conditions for the photochemical reaction are by no means ideal, since the source of energy emits rays which act on the products of the reaction. The ideal condition would of course be the entire exclusion of all rays except those which activate the carbonic acid. This failure to obtain the ideal conditions introduces serious difficulties into all work on photosynthesis, and these difficulties will become more apparent when the later work on this subject is described.

An obvious method of preventing the photochemical decomposition of the formaldehyde would be to introduce into the solution of carbonic acid a substance which absorbs the harmful rays. By direct observation it has been found

that the stability of formaldehyde, when illuminated by the unscreened rays of the quartz mercury lamp, is increased by the addition of certain inorganic compounds; and it may, therefore, be suggested that, in part at any rate, the rôle played by the colloidal ferric hydroxide, etc., in Moore and Webster's successful experiments on the photochemical production of formaldehyde from carbonic acid was protective rather than catalytic.

Many experiments have been carried out in order to determine the best conditions for demonstrating the photochemical production of formaldehyde from carbonic acid. The best method seems to be the formation of a fine spray of carbonic acid solution by means of an atomiser in the neighbourhood of the quartz mercury lamp. The spray falls into a large funnel and there is no doubt about the presence of formaldehyde in the liquid thus collected.

The photochemical reaction, $H_2CO_3 = CH_2O + O_2$, may now be further considered from the point of view of the three stages of the process. In the first stage we have the activation of the carbonic acid molecule by the absorption of the energy quantum, 9.84×10^{-12} erg, which takes place when the substance is exposed to light of the wavelength 2000 Angstroms. In the second stage we have the reaction proper with the formation of the activated molecules of formaldehyde and oxygen. In the third stage previous experience would lead us to believe that these activated resultant molecules lose energy and pass into their normal and non-reactive phases. On the other hand, as was first shown by Moore and Webster, a strong aqueous solution of formaldehyde, on exposure to the light from the quartz mercury lamp, develops the power of reducing Benedict's solution. By the action of the light the formaldehyde molecules are activated, and these activated mole-

cules undergo polymerisation to give compounds which are analogous to the hexose sugars in that they reduce both Benedict's and Fehling's solutions, the light rays which affect this reaction having the approximate wave-length of 2800 Angstroms.[1] Now, it is easy to prove that the reactive phase formed by the action of this light on formaldehyde has the same energy content, and hence the same reactivity, as the reactive phase formed by the action of light on carbonic acid. It is evident that we were incorrect in assuming that the third stage of the latter reaction consists in the loss of energy by the activated formaldehyde to give the normal and non-reactive form. I must confess that we were led astray by basing our expectations too much on previous experience, since the activated molecules produced from activated carbonic acid are characterised by their own specific reactivity, that is, the power of polymerisation to form reducing compounds analogous to the hexose sugars.

Recently the experiments on the action of ultra-violet light on aqueous solutions of carbonic acid have been repeated by Mr. M. R. Johnson in order to determine whether the reducing compounds are formed. The method was exactly the same as was previously described, and it may be stated that in every experiment the production of these compounds was proved. The amount formed is very small indeed and beyond the limit of the Benedict test as ordinarily carried out, but the delicacy of this test is very greatly enhanced if the reaction mixture after being heated for a few minutes is examined, not in ordinary light, but in the light from the quartz mercury lamp. Quantities of cuprous oxide quite invisible in daylight are readily seen in the light from the mercury lamp.

[1] Baly, Heilbron, and Barker, loc. cit.

It may be pointed out here that these reducing compounds must have been directly produced by the action of ultra-violet light on the carbonic acid, and not by the action of the light on the traces of formaldehyde simultaneously formed. Experiments carried out by Moore and Webster, and confirmed in Liverpool, have definitely proved that no reducing compounds are formed photochemically from formaldehyde at concentrations less than 0.5 per cent., and when light acts on carbonic acid the concentration of the formaldehyde produced does not exceed 0.001 per cent.

The smallness of the yield of the reducing compound is due, in part at any rate, to the absence of the ideal conditions previously defined. We have found that carbohydrates and analogous compounds are rapidly decomposed by the rays from a quartz mercury lamp, and consequently, once again, we never can find more than the excess of the amount produced over that decomposed. One of the products of photochemical decomposition of the carbohydrate, and analogous compounds, is ordinary formaldehyde; and thus the presence of ordinary formaldehyde in illuminated solutions of carbonic acid is undoubtedly a secondary product due to the photochemical decomposition of the reducing compounds, which are primary products of the action of light on carbonic acid. The formation of both products, reducing compounds and formaldehyde, afford strong evidence that the reaction, $H_2CO_3 = CH_2O + O_2$, does take place in ultra-violet light.

The foregoing evidence is by no means all that we have obtained in favour of the formation of activated formaldehyde by the action of light on carbonic acid. There is a considerable amount of evidence which is indirect in the sense that compounds formed from the activated formalde-

hyde can be obtained; and, for my own part, I believe this evidence to be of still greater value than that brought forward above.

If an aqueous solution of formaldehyde and potassium nitrite is exposed to the quartz mercury lamp, it becomes alkaline and there is synthesised the compound formhydroxamic acid,

$$\begin{matrix} CHOH \\ \| \\ NOH \end{matrix}$$

This synthesis was first demonstrated by Baudisch who exposed an aqueous solution of potassium nitrite, containing methyl alcohol, to ultra-violet light.[1] No reaction takes place between these two substances in the dark at temperatures below 50°, but at higher temperatures the formaldehyde undergoes the Cannizaro reaction with the formation of methyl alcohol and formic acid. In the light from the quartz lamp formhydroxamic acid is synthesised at room temperatures, and it is thus evident that its formation is due to the combination of the activated formaldehyde with the potassium nitrite. As a photosynthetic product, formhydroxamic acid has the great advantage of giving an insoluble copper salt, the composition of which is perfectly definite. The formation of this compound when activated formaldehyde is produced in the presence of potassium nitrite has been established beyond any doubt by means of the copper salt. When solutions of carbonic acid containing potassium nitrite are exposed to the light from the mercury lamp, formhydroxamic acid again is produced, its presence being established by means of its copper salt.[2] This affords strong evidence in favour of the formation

[1] Ber., *44*, 1009 (1911).

[2] Baly, Heilbron, and Hudson, Trans. Chem. Soc., *121*, 1078 (1922).

of activated formaldehyde by the action of ultra-violet light on carbonic acid.

As will be seen presently from the detailed description of the experiments, mixtures of ammonia and formaldehyde give, under the influence of light, ring compounds containing nitrogen, such as piperidine and coniine. Since it is well known that these compounds are not formed by the action of ordinary formaldehyde on ammonia, their synthesis must be due to the activation of the ordinary formaldehyde by the light. When an aqueous solution of synthetic ammonia, saturated with carbon dioxide, is exposed to the light from the mercury lamp, compounds of the same type are produced, in one case piperidine hydrochloride, m.p. 233–235° being isolated in small quantities. Here, again, we have strong evidence of the formation of activated formaldehyde by the action of light on carbonic acid.

The third series of experiments are of a different type and deal with the action of the silent electric discharge on mixtures of hydrogen and carbon monoxide. As was first noted by W. Loeb, these gases condense to give compounds which reduce Benedict's solution, and recently this reaction has been investigated in Liverpool by Dr. J. H. Jones. We have found that a thick syrup is formed with a very strong reducing power towards Benedict's solution, and that some formaldehyde is simultaneously produced, but there is no evidence as to whether this is a direct or indirect product. Although these results are not exactly similar to those already described, it is of considerable interest that, by the supply of energy to mixtures of hydrogen and carbon monoxide, reducing compounds and formaldehyde are produced, especially since qualitative tests show that

the reducing compounds are analogous to those produced by the polymerisation of activated formaldehyde.

Returning once again to the fundamental reaction, the photochemical conversion of carbonic acid into formaldehyde and oxygen, I may refer to the difficulty caused by the total absence of formaldehyde in the living leaf. It would seem that this difficulty has now been disposed of, since the reaction does not give ordinary formaldehyde but activated formaldehyde which, in the absence of compounds with which it may combine, polymerises to form reducing compounds. The ordinary formaldehyde found in the laboratory experiments is a photochemical decomposition product of the reducing compounds and is not a component of the main reaction. Since the short wave ultra-violet light is not present in the sun's rays ordinary formaldehyde is not formed in the living leaf.

I will take this opportunity, before dealing with the criticism of this work, of describing the major difficulties which beset all these experiments on photosynthesis. I have already referred to one of these, caused by the impossibility of realising the ideal conditions, which results in the photochemical decomposition of the products of the photosynthesis. Not only does this reduce the yield to a very small amount, but it also introduces further complications caused by the presence of the decomposition products. In addition to this, trouble is also introduced by the well-known action of very short wave-length light on water to give hydrogen peroxide. Photochemical oxidation adds its quota to the total difficulties, but we have to a considerable extent succeeded in minimizing this by the use of an Al–Pt couple placed in the reaction mixture.

There is one phenomenon which caused a great deal of trouble in the early stages of the work and which was

entirely unexpected. It was found at one period of our investigations that the results obtained were alarmingly sporadic, being sometimes positive and sometimes negative, where previously they had been uniformly positive. As time went on the results became less and less satisfactory until a stage was reached when no positive result could be obtained, and no explanation of this could be found. One day, however, we found that one or two of the quartz tubes used in the work had developed an amethyst colour exactly similar to that of the natural variety, and obviously it had developed an absorptive power in the visible region. It was also found that the quartz had become opaque to ultra-violet light. On heating at about 500° these tubes developed a very fine green phosphorescence which soon vanished. On cooling, the tubes were found to be colourless and to have regained their transparency to ultra-violet light. On further investigation it was found that the opacity to ultra-violet light commences with the short waves and gradually extends towards the longer wave-lengths, until it finally reaches the visible region when the amethyst colour is developed. Long before the stage of visible colour is reached the quartz has become opaque to ultra-violet light and hence is useless for work on photosynthesis. When the significance of this phenomenon was realised every quartz tube used in the work, both coloured and colourless, was submitted to the heat treatment. Every tube phosphoresced, and when the treated tubes were employed in the photochemical experiments positive results were once again uniformly obtained.

The explanation of this phenomenon is not difficult to find on the molecular phase theory which was brought forward and discussed in my two previous lectures. By absorption of energy at the phase frequency in the extreme

ultra-violet, the phase equilibrium normally present in quartz is displaced, and new, metastable phase equilibria of higher energy content are established, depending on the time of exposure to the light. Since the new phases have higher energy contents, their characteristic frequencies are smaller and are situated in the ultra-violet or visible region. As a result of this the quartz, when in a metastable condition, absorbs the ultra-violet rays and, in the extreme case, some of the visible rays. The time that a quartz tube takes to lose its transparency to the ultra-violet has not been determined, but a tube after it has once become opaque and undergone the heat treatment deteriorates more rapidly than an entirely new tube. If the tubes are in continuous use for photosynthetic work they should be subjected to the heat treatment once every fourteen days.

These observations have some significance in connection with the efficiency of the quartz mercury lamp. These lamps are usually made in one of three types which are designed to operate with continuous current at 100, 220, and 500 volts, respectively. In the case of the 100-volt lamps the temperature attained by the quartz during the operation of the lamp is not high, and as a result the phase change sets in and after a short time the lamp loses its efficiency as a source of ultra-violet light of short wavelength. The temperature attained by the 220-volt lamp is much higher and in this case the new phase equilibrium is not stable, so that this lamp loses little of its efficiency as a source of short wave ultra-violet light. We have had no experience of the 500-volt lamp, but in all probability the temperature reached during operation is higher still, so that the efficiency will not be impaired by continuous use.

At the meeting of the British Association for the Ad-

vancement of Science held at Saskatoon in August, Professor Porter communicated a very important paper on the photochemical conversion of carbonic acid into formaldehyde. In his early experiments he had no difficulty in proving the production of small quantities of formaldehyde when mixtures of carbon dioxide and water vapour were exposed to the light from a quartz mercury lamp. He found, however, that as certain sources of impurities were removed the yield of formaldehyde became progressively less, until in the complete absence of impurities no trace of either formaldehyde or reducing compounds could be detected. He found that the passage of the carbon dioxide through a lubricated stop-cock and through a short length of rubber tubing introduced sufficient impurities to "catalyse" the production of traces of formaldehyde.

These results are of singular importance and present a remarkable analogy with some observations recorded by W. T. Anderson.[1] The photochemical reaction

$$KNO_3 = KNO_2 + O$$

is a familiar one, and it is perfectly possible to demonstrate the presence of nitrite in a solution of potassium nitrate after it has been exposed to ultra-violet light.[2] On the other hand, Anderson has proved that in the complete absence of all impurities the reaction does not take place, but that a photochemical equilibrium is established

$$KNO_3 \rightleftarrows KNO_2 + O$$

in which the amount of nitrite present is very small. When the exposed solution is removed from the radiation, the system reverts back to the nitrate and no nitrite can be detected. In the presence of oxidisable impurities one of

[1] J. Amer. Chem. Soc., *46*, 797 (1924).
[2] Moore and Webster, Proc. Roy. Soc., *90, B*, 158 (1919).

the components of the equilibrium is removed, and, therefore, the reaction will proceed from left to right when illuminated with light of the frequency characteristic of the nitrate.

The case of carbonic acid seems to me to be exactly analogous in that one molecule is photochemically converted into two molecules, one of these being oxygen. It may reasonably be suggested, therefore, that, in the complete absence of impurities, the illumination of a solution of carbonic acid will establish a photochemical equilibrium

$$H_2CO_3 \rightleftarrows CH_2O + O_2$$

in which the amount of activated formaldehyde is very small. If that is so, then, on removal of the illuminated solution from the radiation, the system will revert to carbonic acid and no formaldehyde or reducing compounds will be found.

It is a simple matter to put this suggestion to the test of experiment, since, if either of the components on the right-hand side be removed, the reaction will proceed from left to right. The removal of the oxygen can readily be effected by the addition of easily oxidisable impurities such as those very impurities Porter found were able to promote the reaction. It is also possible to remove the activated formaldehyde, since we know from independent observations that it combines with potassium nitrite to produce formhydroxamic acid. In the presence of potassium nitrite, therefore, the reaction should proceed from left to right with the formation of formhydroxamic acid. I have already described how formhydroxamic acid is actually produced when aqueous solutions of potassium nitrite, saturated with carbon dioxide, are exposed to short wave-length ultra-violet light.

The experimental evidence, therefore, supports the view that in the pure state a photochemical equilibrium is established when carbonic acid is illuminated and that the reaction will not proceed unless one or both of the components on the right-hand side are removed from the equilibrium. It may here be pointed out that in the case of the living plant the oxygen is removed, since it enters into combination with the pigments and remains in some form of combination until, finally, it is transpired into the atmosphere through the stomata.

The negative results obtained by Porter would seem to have a special value in that they have led to the realisation of the existence of the photochemical equilibrium, $H_2CO_3 \rightleftarrows CH_2O + O_2$. They have led also to the correlation of various experimental results which afford a convincing proof of this equilibrium, and at the same time they give a second reason why the yield of the reducing compounds is so small when carbonic acid is illuminated, while the yields of the compounds formed by combination of the activated formaldehyde with other substances are relatively large. The existence of the photochemical equilibria with carbonic acid and with potassium nitrate is a matter of considerable theoretical interest, but this aspect of Anderson's and Porter's experiments cannot be discussed here.

Up to the present the photochemical production of activated formaldehyde only has been discussed from the point of view of the activation of the carbonic acid molecule by light of its phase frequency in the short wave ultra-violet region. When the conditions are considered under which this photochemical reaction is brought about in the living leaf, it is manifest that light of that frequency is not the activating agent, since it is well known that sunlight con-

tains no rays of such short wave-length. The problem of natural photosynthesis cannot be completely solved until an explanation is found of the mechanism utilised by the living leaf.

For our knowledge of the chemistry of the pigments which are present in the living chloroplast, and which undoubtedly form the basis of the photosynthetic mechanism, we are indebted to Willstätter. There are present four pigments, namely chlorophyll A, $C_{55}H_{72}O_5N_4Mg$; chlorophyll B, $C_{55}H_{70}O_6N_4Mg$, H_2O; carotin, $C_{40}H_{56}$; and xanthophyll, $C_{40}H_{56}O_2$. The difference between chlorophyll A and chlorophyll B is just one molecule of oxygen and it is difficult to believe that this is purely fortuitous in view of Willstätter's statement that chlorophyll A forms an addition compound with one molecule of carbonic acid. Indeed Willstätter himself was the first to suggest the possibility that this addition compound, on exposure to light, is converted into formaldehyde and chlorophyll B in accordance with the equation

$$C_{55}H_{72}O_5N_4Mg, H_2CO_3 = C_{55}H_{70}O_6N_4Mg, H_2O + CH_2O.$$

In the hopes of proving the truth of this suggestion Willstätter investigated the ratio between the amounts of the two chlorophylls during photo-assimilation of carbon dioxide, fully expecting to find that the ratio of chlorophyll B to chlorophyll A increased. He found, however, that the ratio remains constant and as a result of this he felt obliged to abandon his theory.

On the other hand, the relation between carotin and xanthophyll as regards oxygen is exactly the same as between the two chlorophylls, and consequently it is reasonable to suggest that carotin has the power of reducing chlorophyll B to chlorophyll A, itself being converted into xanthophyll.

The objection found by Willstätter in the constant ratio between the two chlorophylls now disappears, since the change in this ratio caused by the process represented in the equation above will be restored by the reduction of the newly formed chlorophyll B by the carotin. The place to look for change during photo-assimilation of carbon dioxide will be in the xanthophyll-carotin ratio which should tend to increase. This increase was actually found by Willstätter, but he did not link it up with his first suggestion regarding the function of the chlorophylls.

In view of this last mentioned observation by Willstätter I venture to suggest that the plant mechanism is a four component system involving three separate reactions as follows:

1. $C_{55}H_{72}O_5N_4Mg, H_2CO_3 = C_{55}H_{70}O_6N_4Mg, H_2O + CH_2O.$

2. $C_{55}H_{70}O_6N_4Mg, H_2O + C_{40}H_{56} = C_{55}H_{72}O_5N_4Mg + C_{40}H_{56}O_2.$

3. $C_{40}H_{56}O_2 = C_{40}H_{56} + O_2.$

The final stage in which the xanthophyll is reduced to carotin must be effected with the help of an oxygen carrier, since the oxygen is not set free within the chloroplast but is translocated in the combined state through the leaf and transpired into the atmosphere through the stomata.

Two important points at once arise on this suggestion, first, the possibility of putting this scheme to the test of experiment and, second, the energy relations of the whole process. As regards the experimental proof, it may be said at the outset that one essential difficulty presents itself, namely, that of the solvent. Willstätter has shown that the properties of the two chlorophylls differ very materially in true and colloidal solution, and we have not yet succeeded in solving the problem. I may say, however, that

we have succeeded in establishing the reality of one step in the above scheme, namely, the oxidation of carotin into xanthophyll. Dr. Barker, Dr. Stead, and Dr. Robertson, working in Liverpool, have found that carotin in chloroform solution is oxidised by atmospheric oxygen, especially in light, to xanthophyll, the change having been proved by absorption spectra measurements. On the cautious addition of a solution of anhydrous ferric chloride in acetone to a solution of carotin in acetone, xanthophyll is also produced. In this case the xanthophyll was separated by the Tswett method of chromatographic analysis. This result is very encouraging, but as yet we have not succeeded in reducing xanthophyll to carotin. Many reducing compounds were tried, but it was found that either no action took place or the reduction was carried too far.

The energy relations are of peculiar importance, for we have already seen that in order to activate a molecule of carbonic acid, so that it may react to give activated formaldehyde and oxygen, a quantum of energy is required which is about 9.84×10^{-12} erg, and the question arises as to whether the pigments are able to supply this energy increment by absorbing their characteristic and smaller quanta of energy in the visible region. Of the three reactions specified above, the third may be ignored, since we know from Willstätter's observations that the ratio of xanthophyll to carotin tends to increase during photo-assimilation, and, therefore, the third reaction cannot play an integral part in the activation of the carbonic acid. Considering the first two reactions, we have three pigments on the left-hand side which must be activated, namely, chlorophyll A, chlorophyll B, and carotin. Now the absorption bands of these compounds differ to a certain extent in different solvents and we have no accurate measurement of the central

wave-lengths of the bands characteristic of the pigments in the chloroplast. In chloroform solution the central wave-lengths of the absorption bands of the two chlorophylls are 6670 and 6480 Angstroms, respectively, whilst the principal absorption band of carotin has a central wave-length of 4630 Angstroms. The characteristic quanta absorbed by the three compounds are, therefore, 2.95×10^{-12}, 3.04×10^{-12}, and 4.25×10^{-12} erg, respectively. The sum of these three quanta is 10.24×10^{-12} erg which only differs from the quantum required to activate the carbonic acid molecule, namely, 9.84×10^{-12} erg, by 4 per cent. The three pigments, therefore, are able to absorb just the right amount of energy to activate the carbonic acid molecule, and, since we have an equilibrium condition between the three pigments with the carbonic acid in combination with one of them, we are safe in stating that the carbonic acid will be activated. The activated carbonic acid will at once react to give activated formaldehyde, since no question arises as to the photochemical equilibrium referred to on page 80 owing to the fact that the oxygen is not set free but remains in combination. On the other hand, further evidence of the reality of the photochemical equilibrium is to be found in the behaviour of the living plant, since photo-assimilation ceases if the plant is placed in oxygen under a pressure of two atmospheres.

The process detailed above, in which the light energy necessary for activating a substance is absorbed at frequencies other than those characteristic of the principal reactant, has been called photocatalysis, and a special case of this phenomenon has been studied by Daniels and Johnson.[1] I venture to believe that in the results detailed above, an explanation has been found of the mechanism

[1] J. Amer. Chem. Soc., *43*, 72 (1921).

whereby photo-assimilation of carbon dioxide takes place in the living leaf. The results obtained in the laboratory with ultra-violet light afford convincing evidence that in the photochemical reaction formaldehyde is produced in an activated condition, and that, in this state, it possesses a reactivity which is entirely different from that observed in the laboratory under the ordinary methods of activation. The usually observed reactivities of this substance are those of phases of lower energy content than the phase which results from carbonic acid activated by its abnormally large energy increment. The highly activated formaldehyde obtained from carbonic acid does not lose energy to give ordinary formaldehyde (which therefore is not present in the living leaf) but undergoes certain definite reactions, two of which have been specified, namely, its ready polymerisation to give reducing compounds and its combination with potassium nitrite to give formhydroxamic acid.

An interesting feature of the photocatalytic production of activated formaldehyde in the living leaf and its subsequent reactions to give many of the products of plant life may be mentioned. I have already referred to the difficulties, associated with laboratory experiments on photosynthesis, which arise from the decomposition of the products by harmful rays emitted by the light force employed. This is not the case in the leaf where the photochemical conditions from this particular point of view are ideal.

I will now describe in detail the investigations we have made of the reactions characteristic of the activated formaldehyde, and will first deal with its polymerisation and the products formed in this reaction. In studying this process we have prepared the activated formaldehyde by the action of light on a concentrated aqueous solution of

ordinary formaldehyde. In the first place, Mr. H. G. Littler has determined the conditions for obtaining the best yield of the reducing compounds with a given intensity of the activating light, and the two most important controlling factors are the hydrogen ion concentration and the temperature. When the formaldehyde solution is exposed to the light the formation of the reducing compounds commences at once, but at the same time the solution develops an acidity due to secondary reactions. The yield of the reducing compounds is materially decreased in acid solution, and we further found that the yield is less in an alkaline solution than in a neutral solution. In order to neutralise the acid by-products it is necessary to have present an insoluble base which will react with them. Very many substances were tried and by far the best yield of reducing compounds is obtained if an excess of precipitated magnesium carbonate is present. When this reacts with the acids, carbon dioxide is set free, with the result that the final condition is obtained of a saturated solution of magnesium bicarbonate. The hydrogen ion concentration of this solution, judging from a considerable number of trials, is exactly the right condition for obtaining the best yield.

The use of precipitated magnesium carbonate, however, gives rise to an unexpected difficulty, since, when the concentration of the reducing compounds reaches a value of about 2 per cent., calculated as glucose, the carbonate dissolves in the solution and is photochemically deposited on the walls of the reaction vessel where the light enters the solution. This layer effectively protects the solution from the light and it becomes necessary to dismantle the apparatus and remove the layer by treatment with mineral acid, an operation which must be repeated at regular intervals. If calcium carbonate is substituted for the magnesium salt,

this action does not take place and, therefore, much time is saved. We have found that, in spite of the fact that the yield of reducing compounds obtained with the hydrogen ion concentration of a saturated solution of calcium bicarbonate is as much as 20 per cent. smaller, the time taken to obtain the same yield of reducing compounds is about the same in the two cases. In actual practice, therefore, we use precipitated calcium carbonate as the neutralising agent.

The remarkable influence of small differences in hydrogen ion concentration is a matter of considerable interest in view of the elaborate mechanism of buffer solutions in the living plant, obviously designed to maintain constant conditions of hydrogen ion concentration. It is probable, also, that this is a factor which controls all the reactions of activated formaldehyde, and not only its polymerisation. Again, it may be suggested that the special value of a saturated solution of magnesium bicarbonate is connected with the use of chlorophyll containing magnesium, particularly since Willstätter found that the chlorophyll A-carbonic acid complex in the free state gives magnesium carbonate on exposure to light. It may, very possibly, be the case that the decomposition is inhibited in the plant by the presence of magnesium bicarbonate in the chloroplast.

It is hardly necessary to point out that blank tests carried out with both magnesium carbonate and calcium carbonate and with formaldehyde in the absence of light have proved that no reducing compounds are formed. For example, a strong aqueous solution of formaldehyde, containing precipitated magnesium carbonate, gave no trace of reducing compounds after remaining in the dark for six weeks.

We have found it possible to carry out the photosyn-

thesis of the reducing compounds on a reasonably large scale by the use of a rectangular glass tank 15 inches square and 8 inches deep. Each of the four walls of the tank is drilled with a circular hole 2.25 inches in diameter, the centres of these holes being three inches from the bottom of the tank. In each hole a quartz tube, 6 x 2 inches, and closed at one end, is mounted as shown in Fig. II. About 20 litres of 40 per cent. formaldehyde solution is placed in the tank and a U-shape quartz mercury lamp is pushed into each of the quartz tubes. Cooling coils are mounted

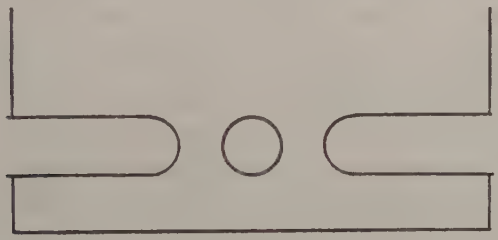


Fig. II.

in the tank and a constant stream of water is maintained through them. By controlling this stream of water any desired temperature can be obtained, and after many trials we found that the optimum temperature is about 37°. The tank is covered with a plate glass lid drilled with holes for the inlet and outlet water tubes, and a central hole for the rod of a stirring apparatus. During the exposure precipitated calcium carbonate is added from time to time so that it is always present in excess. Constant stirring is not maintained, as sufficient circulation is caused by the convection currents set up by the heat of the quartz lamps. An additional and necessary precaution may be mentioned, which must be taken in order to obtain the best yields. The very short wave ultra-violet rays from the lamps are

absorbed by atmospheric oxygen, which is thereby converted into ozone, and it happens that the absorption band of ozone is very near to that of formaldehyde. This reaction, which takes place within the two-inch quartz tubes, lessens the yield of the reducing compounds within the tank for two reasons. The formation of the ozone decreases the oxygen concentration, and thus allows more of the very short wave-length rays to pass into the solution and decompose the reducing compounds; and, further, the ozone absorbs some of the rays which activate the formaldehyde. A steady current of air is therefore passed into each of the two-inch tubes, and care must be taken that this current is not too rapid, since the efficiency of the lamps is materially reduced on cooling.

The amount of reducing compounds present is estimated every twelve hours and this reaches a maximum at about 6 per cent., calculated as glucose, since at this concentration the velocity of the photochemical decomposition of these compounds equals their velocity of formation. This maximum reducing power is reached with continuous illumination in about 14 days, there being present about 1200 grams of reducing compounds, in terms of glucose.

For the following method of separation of the reducing compounds from the unchanged formaldehyde, calcium salts, etc., we are indebted to Mr. Littler. The greater part of the formaldehyde is removed by evaporation under reduced pressure at 70°, a slow stream of air being continuously passed through the liquid, until the total volume is reduced to about 4 liters. During this operation a considerable amount of the formaldehyde undergoes the Cannizaro reaction to give formic acid and methyl alcohol; in order to neutralize the free acid, an excess of precipitated calcium carbonate is added before commencing the operation.

On addition of absolute alcohol to the concentrated liquid, the greater proportion of the calcium salts separates out. The filtrate is again concentrated under reduced pressure, in the presence of calcium carbonate, and again diluted with absolute alcohol, this being repeated until no further separation of calcium salts takes place. One of the photochemical decomposition products of the reducing compounds is glucuronic acid, and a special treatment is necessary to remove this compound since the calcium salt is soluble in alcohol. An exactly equivalent quantity of zinc sulphate in aqueous solution is added and the calcium sulphate removed by filtration. The filtrate is concentrated under reduced pressure in the presence of zinc carbonate, absolute alcohol is added, and the zinc glucuronate removed by filtration. This process is repeated until the zinc salt has been entirely removed.

The final filtrate is reduced in volume to a suitable concentration and chloroform is added, when the reducing compounds separate in the form of a thick syrup, which is collected, taken up in absolute alcohol, and again precipitated with chloroform. This process is repeated until the syrup is obtained free from formaldehyde. The small quantity of chloroform mixed with the syrup is removed by gentle heat under reduced pressure.

Thus prepared, the syrup is very viscous, transparent, and amber in colour. It exhibits a green fluorescence, is very sweet to the taste, and has a reducing power of 30–35 per cent., calculated as glucose. In a preliminary investigation of the syrup, attempts were made by Dr. Barker and Dr. Francis to prove the presence of hexose sugars by the process of exhaustive methylation. The results obtained were encouraging, since a small quantity of a methylated derivative was obtained, containing 60 per cent.

OCH_3, which corresponds to that of a penta-methylated hexose. Formation of glucuronic acid is also of importance as evidence of hexose formation. Careful qualitative tests established the total absence of trioses and pentoses, non-formation of the latter being of considerable interest.

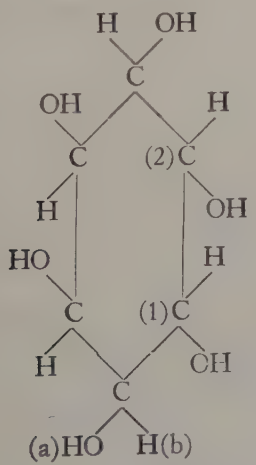
We are indebted to Principal Irvine, of St. Andrews, who, in conjunction with Dr. Francis, has carried out a systematic investigation of the photosynthesised syrup with the view of determining whether or no hexoses are present. Valuable evidence of their presence was first obtained in the formation of a methyl hexoside, and subsequently, by exhaustive methylation, they succeeded in preparing tetra-methyl glucose. These results prove that there is present in the syrup about 10 per cent. of an aldose, probably glucose. This accounts for rather less than one-third of the total reducing power of the syrup, and the investigation of the remaining compounds is being actively pursued.

The proof that glucose is one of the products of the polymerisation of active formaldehyde is of considerable importance, since it establishes the fact that it is possible in the laboratory to reproduce the process taking place in the living plant to as far as the formation of one of the naturally occurring hexoses. The total absence of pentoses in our photosynthetic syrup indicates that these compounds in the living plant are not the direct products of photosynthesis, but that they are formed indirectly from hexoses or their condensation products, the starches and celluloses. The production of a hexose in preference to a pentose or triose, when activated formaldehyde polymerises, raises the very interesting question of the mechanism of this polymerisation, since it would be expected on the grounds of probability that the chances against hexose formation are the greatest. I venture to suggest the following mechanism as an explanation of the process.

In view of the remarkable reactivity of activated formaldehyde it seems to me that it is necessary to picture a different formula from that given to ordinary formaldehyde. This abnormal reactivity is well expressed by the Nef formula, $C\begin{smallmatrix}H\\OH\end{smallmatrix}$, with the carbon atom bivalent. The formation of formhydroxamic acid, for example, by the union of activated formaldehyde with potassium nitrite can at once be understood

$$CHOH + KO - N = O = \begin{matrix}CHOH\\ \|\\ KO - N = O\end{matrix} = \begin{matrix}CHOH\\ \|\\ KO - N\end{matrix} + O.$$

In the absence of compounds with which to combine, the substance CHOH will strive to attain two conditions, the most stable configuration possible and quadrivalence of the carbon atom. It may be accepted from the space lattice formulæ of diamond and graphite that the most stable configuration is the six-membered ring, and consequently by the polymerisation of six molecules of activated formaldehyde to form the ring compound



both aspirations will be satisfied. This molecule when freshly synthesised will be reactive, so we are justified in attributing to it properties such as are common in the experience of organic chemists. There are four changes which this molecule can undergo without introducing any novel properties:

1. The loss of water which, if the loss be symmetrical, will entail the loss of three molecules with the formation of phloroglucinol.
2. The migration of the hydrogen atom (a) to the carbon atom (1) and rupture of the ring to give the open chain formula of glucose.
3. The migration of the hydrogen atom (a) to the carbon atom (1) and of the hydrogen atom (b) to the carbon atom (2) with rupture of the ring to give the open chain formula of fructose.
4. The loss of energy by the molecule to give the non-reactive compound, inosite.

There are, therefore, four possible derivatives which in this way will be formed by the polymerisation of activated formaldehyde, namely, phloroglucinol, glucose, fructose, and inosite. All four substances are formed in the living leaf, and it would seem to be highly probable that they are all photosynthetically produced from carbonic acid through activated formaldehyde. It is to be expected, therefore, that all four substances should be present in the photosynthetic syrup prepared in the laboratory. The presence of one of these, glucose, has already been established, but Irvine has not been able to find any evidence of a ketose. Since fructose is less stable than glucose, the velocity of its photochemical decomposition will be greater than that of glucose, and consequently its absence from the syrup does not prove that it is not formed. Irvine is

of the opinion that a polyhydric phenol is present in the syrup, and we have obtained in Liverpool some evidence of the presence of a non-reducing hexose which gives the iodoform reaction. The further investigation of this syrup is being actively pursued and I have great hopes that still more evidence will be found in support of the above suggested mechanism of the polymerisation of activated formaldehyde.

We may now turn our attention to the problem of the photosynthesis of nitrogen compounds. It is known that the living plant obtains its supply of nitrogen from the nitrates of potassium and calcium, and also from ammonium salts. During their translocation from the roots to the leaves, the nitrates are reduced to nitrites, and, since it has been established that activated formaldehyde at once reacts with nitrites, it may be suggested that many of the nitrogen compounds found in plants are the direct products of photosynthesis. In order to test the truth of this suggestion a considerable amount of work has been carried out on the action of activated formaldehyde on nitrites and on ammonia with very promising results, since in both cases evidence has been obtained of the production of naturally occurring nitrogen compounds.

We may first deal with the action of activated formaldehyde on ammonia, a preliminary account of which has already been published.[1] Solutions of formaldehyde and specially purified ammonia were exposed to the light from the quartz mercury lamp for many hours, during which the solutions turned brown in colour. After a sufficient period of illumination had elapsed, the excess of formaldehyde was removed by repeated evaporation with fuming hydrochloric acid. Finally the dry hydrochlorides were

[1] Baly, Heilbron, and Stern, Trans. Chem. Soc., *123*, 185 (1923).

extracted with absolute alcohol, and the soluble hydrochlorides were again taken up in alcohol and fractionally precipitated with ether. In the end small quantities of a crystalline salt were obtained, which was the hydrochloride of a liquid base with the same odour as coniine. The hydrochloride gave all the well known alkaloidal reactions and the following tests specifically characteristic of coniine. It formed a double salt with potassium cadmium iodide, indistinguishable under the microscope from the same double salt prepared from the natural alkaloid. It gave with Dilling's modification of Melzer's test [1] the colour reactions which are specific for coniine. In addition to these, the photosynthesised alkaloid, gave the unmistakable odour of butyric acid on oxidation with potassium dichromate and sulphuric acid. Finally, its physiological action was the same as that of natural coniine.

This result was subsequently criticised by Snow and Stone,[2] who suggested that the substance was not coniine but tetramethylmethylenediamine, formed by the Werner reaction between ammonium chloride and formaldehyde. In support of this suggestion these authors showed that this base has the same physiological action as coniine and gives certain qualitative tests similarly to coniine, but not the two specific tests mentioned above. It is surprising that in putting forward this suggestion Snow and Stone ignored the fact that no Werner base could possibly have survived the repeated evaporation with concentrated hydrochloric acid, since these compounds are quantitatively hydrolysed by acid to formaldehyde and methylamine and dimethylamine. On this ground alone their criticism fails

[1] Arch. Pharm., *236*, 701 (1898).
[2] Trans. Chem. Soc., *123*, 1509 (1923).

and further work has given results which conclusively disprove their contention.

The investigation of the influence of light on mixtures of ammonia and formaldehyde has been repeated by Dr. Edith Morrison with an improved technique, including the use of the Al–Pt couple in order to eliminate photochemical oxidation as far as possible. In view of the peculiar difficulties of the identification of coniine in small quantities, it was decided to prove the intermediate formation of piperidine and subsequently to study the action of activated formaldehyde on this compound. Aqueous solutions of synthetic ammonia [1] and formaldehyde were exposed for several days to the rays from the quartz mercury lamp, an Al–Pt couple being placed in each reaction vessel. The resulting solution was repeatedly evaporated with concentrated hydrochloric acid until all the Werner bases had been completely hydrolysed. During this operation considerable quantities of ammonium chloride, methylamine and dimethylamine hydrochlorides separated out and were removed by filtration. The whole of the dry hydrochlorides were extracted with absolute alcohol, and the filtrate was evaporated to dryness and again extracted, until all the ammonium chloride was removed. A similar treatment was given with chloroform until all the methylamine hydrochloride was removed, this salt being insoluble in chloroform. The remaining mixture of hydrochlorides was again evaporated with fuming hydrochloric acid, once or twice, in order to decompose any possible residue of Werner base. The resulting mixed hydrochlorides, on the addition of alkali, now gave the unmistakable odour of

[1] The most rigid tests proved the total absence of all organic bases from this ammonia, for the gift of which we are indebted to Messrs. Brunner Mond, Ltd.

piperidine, and the following method was adopted of separating the piperidine from the dimethylamine and trimethylamine and also any coniine associated with it.

The mixed bases were set free by the addition of alkali, taken up in ether and the ethereal solution was gently warmed in order to drive off as much as possible of the two alkylamines. After cooling, dry hydrogen chloride was passed into the ether, when moist crystals separated out, and these were collected and evaporated to dryness with fuming hydrochloric acid. To an aqueous solution of the hydrochlorides gold chloride was added and, since dimethylamine and coniine do not form insoluble aurichlorides, the insoluble precipitate thereby obtained could only be the aurichlorides of piperidine and trimethylamine. The percentage of gold in this precipitate corresponded to a mixture of 92 per cent. of piperidine and 8 per cent. of trimethylamine. The following melting points were obtained, the aurichloride being used in each case

Piperidine	232.5–233.5°
Trimethylamine	243 –244°
50 per cent. Trimethylamine and 50 per cent. Piperidine	218 –229°
8 per cent. Trimethylamine and 92 per cent. Piperidine	230.5–231.5°
The last with more Piperidine	232.5–233.5°
Photosynthesised material	231.5–232.5°
Photosynthesised material and Piperidine	232.5–233.5°

This method of mixed melting points leaves no doubt of the reality of the photosynthesis of piperidine from ammonia and formaldehyde; and, therefore, additional evidence in favour of our original synthesis of coniine has been obtained. By the action of activated formaldehyde on piperidine more complex compounds are obtained, the nature of which is still under investigation.

I have already referred to the photosynthesis of formhydroxamic acid by the action of activated formaldehyde on potassium nitrite, this having been first discovered by

Baudisch and fully confirmed in Liverpool. Mention may be made of the action of ultra-violet light on a solution of calcium nitrite in absolute methyl alcohol, which has recently been studied by Dr. Elwin Roberts. As is well known, short wave-length ultra-violet light decomposes methyl alcohol into formaldehyde and, probably, hydrogen, and consequently this method gives a convenient source of activated formaldehyde. The calcium nitrite solution in methyl alcohol, on exposure to the light from the quartz mercury lamp, deposits calcium formhydroxamate, together with some adsorbed nitrite, and the yield is almost quantitative. This result is important since it justifies our studying the further course of the reaction by acting on formhydroxamic acid, prepared from hydroxylamine and ethyl formate with activated formaldehyde. In a previous paper [1] it was stated that the photosynthetic process follows two courses, namely, the production of α-amino acids and the production of nitrogen bases. Amongst the latter, glyoxalin and piperidine have been recognised. Evidence was obtained also of the condensation of individual compounds from each group to form substituted α-amino acids, similar to those obtained by the hydrolysis of the proteins. The hope was expressed at that time that it should be possible to carry the photosynthesis further and obtain substances of a complex structure approaching that of the proteins themselves.

This work has been repeated and extended by Dr. H. L. Saunders, and many new and interesting results have been obtained, one of which may be described. Aqueous solutions of formhydroxamic acid and formaldehyde are exposed to the light from the quartz mercury lamp for eleven days, constant hydrogen ion concentration being

[1] Baly, Heilbron, and Hudson, Trans. Chem. Soc., *121*, 1078 (1922).

maintained by an excess of precipitated magnesium carbonate. After removal of excess of formaldehyde by distillation, about 0.5 gram of a substance is obtained, which is very soluble in water and insoluble in all the usual organic solvents. This compound does not give any characteristic qualitative tests for α-amino acids, etc., but it contains nitrogen and forms a moderately stable hydrochloride. This salt gives an insoluble double salt with gold chloride, which has been analysed. By determination of the gold content the equivalent of the base was found to be 220, and further, 220 parts contain 35 parts of nitrogen. It follows that the minimum molecular weight of the compound is 440 and that in that minimum weight there are 5 atoms of nitrogen. This, in itself, is evidence of the complexity of the products which can be produced by photosynthesis from potassium or calcium nitrite and activated formaldehyde.

Since this compound evolves ammonia on boiling with sodium hydroxide, its hydrolysis by hydrochloric acid was studied. Dilute acid has no action, but on prolonged boiling with concentrated acid hydrolysis takes place, and amongst the products the presence of an α-amino acid has been recognised. It is possible that this acid is histidine, since it gives the colour reactions with diazobenzenesulphonic acid identical with those given by natural histidine. Since the original compound, before hydrolysis, gives no reactions for α-amino acids, the suggestion may be made that it is a condensation product of two or more α-amino acids, and that it marks a further stage towards the photosynthesis of a protein. It is of some interest, therefore, that the compound gives insoluble products with all the usual reagents for proteins, including basic lead acetate,

potassium dichromate, potassium ferrocyanide, Millon's reagent, etc.

The above results afford strong support to the view that the activated formaldehyde, produced photochemically in the living leaf, not only undergoes polymerisation to give hexoses, but also reacts with nitrites and ammonium salts to give α-amino acids and nitrogen bases, these in each case being the first products of the various reactions. As the result of the high energy content of these compounds when first synthesised, they are endowed with great reactivity and undergo condensation to give compounds which are actually found in nature. Direct evidence of such condensation has been found in the case of the α-amino acids and nitrogen bases. Arising from this view some attractive possibilities suggest themselves, one of which may perhaps be mentioned. It is known that certain bases, such as piperidine, do not enter into the constitution of proteins; that is to say, they do not condense with α-amino acids to form substituted α-amino acids. On the other hand, we have found that piperidine is formed by the action of the activated formaldehyde on ammonia and also on formhydroxamic acid, and we may, therefore, conclude that it is formed in the living plant. The plant thus produces bases which it cannot use in making protein, and the suggestion may be made that it converts these unwanted children of photosynthesis into alkaloids by the further action of activated formaldehyde. More generally, it may be suggested that, even though the plant may have learnt how to make use of the alkaloids, these compounds represent the final non-toxic end-products obtained, under the particular conditions existing in the various species, by the action of activated formaldehyde on those bases which are toxic and cannot be utilised in the making of proteins. This sug-

gestion draws attention to the remarkable constancy of alkaloid production both as regards nature and amount in each species of plant. In view of the importance of hydrogen ion concentration in the polymerisation of activated formaldehyde, it is very possible that the nature of the alkaloid produced is also governed by the hydrogen ion concentration. Obviously, therefore, all experiments on photosynthesis with activated formaldehyde should be carried out under absolutely constant conditions of hydrogen ion concentration, as otherwise complex mixtures of different alkaloids will be obtained. This necessity was not realised in the earlier experiments, and a systematic investigation on these lines is now being carried out.

It is evident from what has already been said that when activated formaldehyde is produced in the presence of a nitrite the two substances react together and that this reaction takes precedence of the polymerisation to form hexoses. We have found, however, that if the concentration of the nitrite is small, compared with the amount of activated formaldehyde which is being produced, both reactions take place simultaneously; that is to say, reducing sugars and nitrogen compounds are synthesised at the same time. This is a condition which obtains in the living leaf, and there is no difficulty in understanding how the two processes take place concurrently. The photosynthetic production of nitrogen bases from activated formaldehyde and ammonia or nitrites must be accompanied by the evolution of oxygen over and above that associated with the formation of the activated formaldehyde from carbonic acid. If, therefore, the living plant produces nitrogen bases by photosynthesis, the amount of oxygen transpired into the atmosphere during the photo-assimilation of carbon dioxide must be greater than that expressed by the

molecular ratio $O_2/CO_2 = 1$. It is of considerable interest therefore that the actual value of this ratio as determined by Willstätter is 1.05.

At the commencement of this lecture I laid some stress on the possibility that the chemical processes associated with a reaction of the second class (a reaction with a very large activating increment of energy) might be very different from those with which we are familiar from our long experience of reactions of the first class. I think I was justified in making that statement, for there is no doubt that the photochemical conversion of carbonic acid to formaldehyde is a reaction of the second class and that the subsequent reactions, although few have as yet received the study they deserve, are of a somewhat novel type. The formation of glucose and the synthesis of piperidine may be classed as different from the reactions of every-day chemistry. Similarly, also, the condensation of α-amino acids with certain nitrogen bases to form substituted α-amino acids is outside the practical experience of organic chemists. It has long been realised that in the living plant hexoses condense together to give sucrose, starches, and celluloses, whilst bases and amino acids condense together to give first the substituted amino acids and then the proteins. Our ignorance of the forces at work has led at times to a belief in something mysterious, something perchance inexplicable, which is associated with life, for the whole is so strange to us in spite of the great advances made by the pioneers in organic research.

In a spirit of true reverence for Dame Nature and of high appreciation of her work, I have attempted to show you that the chemistry of the living plant may be but a chemistry of high energy. The great initial stimulus given to the carbonic acid by the energy which the sun pours

upon the earth inaugurates a series of chemical changes. Each and all of these form part of a sequence of events, every step of which marks an energy loss whereby the molecules come nearer and nearer to the states that are familiar to us. We have knowledge of the inorganic compounds from which the story starts, we have knowledge of the products where the story ends, but between the two there lies a tale of high energy, a tale of molecular derring do which the dull chemistry of the test-tube and beaker fails to envisage—and thus has been born the germ of mystery. I beg you not to hug this mystery as sacrosanct, but rather find delight in the romance of molecules, not so far removed from the romances of our youth which taught us all to emulate the noble deeds of men inspired by love and high ideal. I beg you find romance in the noble deeds of molecules inspired by light and high energy, for after all what nobler deed can there be than to promote and sustain life?

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